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A REVIEW OF VOC EMISSIONS AND DRYING MECHANISMS FOR INTERIOR PAINTS AND COATINGS

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EXECUTIVE SUMMARY

This report reviews research into the release of volatile organic compounds (VOCs) from paints and coatings from two perspectives: (a) drying and film formation, and (b) VOC emission into indoor air. The former has been investigated by the paint industry for some decades, especially in relation to understanding drying mechanisms to assist product formulation and development. The latter is of more recent interest and is directed to predicting and controlling the impact of VOC emissions from paints and coatings on indoor air quality. This requires an understanding of VOC emission mechanisms and the review aims to identify knowledge gained from paint drying studies to assist in current VOC emission research. A primary aim is to act as an information resource for industrial and environmental researchers.

The review is based on 120 key references published over the last 30 years. The focus is traditional water-based latex paints and solvent-based coatings for use in buildings rather than novel industrial coatings of recent years. The coating process and drying mechanisms are reviewed for each of these. This includes a limited review of volatile paint constituents and their health hazards.

Solvent-based coatings form semi-dry films by volatility-limited evaporation, similar to neat solvent, but this process is complicated for multi-solvent systems due to compositional changes and molecular interactions. Evaporation rate drops sharply at around 50% of v/v resin content as diffusion becomes the rate-limiting process. "Solidified" coatings may contain 20% v/v solvent. Molar volumes of solvent molecules are then critical to the evaporation process, not solvent volatility. Solvent diffusion coefficients in the resin, solvent concentration and glass transition temperature of the solvent-resin system are important parameters to diffusion-limited evaporation. Drying of water-based latex paints is complicated by latex particle transport and coalescence and the effect of relative humidity on the volatile loss of water c.f. solvent. Latex paints are formulated with specific solvents that will evaporate slowly so that they are retained to assist latex particles to coalesce and form a continuous film, a process that may take several days. Subsequent diffusion-limited evaporation of the coalescing solvent is necessary to form a durable film and may be influenced by a plasticising effect of residual water, an effect not present in solvent-based coatings.

VOC emission studies have focussed on mathematical modelling of the emission process and sink effects of interior surfaces of experimental chambers or building interiors. Many studies have involved only semi-dry films and recent but limited studies have evaluated both wet and semi-dry films and empirical models appropriate to VOC emissions. Theoretical predictions of volatility- and diffusion-limited emission dynamics have been made but non demonstrated experimentally for both processes. Research into volatility-limited emission from several wet sources was able to model the behaviour of non-film forming sources (stain, wax) but not late-stage behaviour of a polyurethane coating, probably due to diffusion becoming the predominant mechanism.

The report concludes with directions for future research. The relevance of volatility or diffusion to the emission process and its dynamics needs to be clarified, especially when selecting appropriate coating conditions (substrate, thickness, loading ratio, environmental conditions) to simulate the built environment. The role of air velocity to evaporative flux from wet coatings needs better understanding; investigation has been limited but free convection at an evaporating surface may better simulate air velocity at an interior surface than a forced air velocity.

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ABSTRACT

This report reviews research studies into volatile organic compound (VOC) emission from interior paints and coatings. A primary aim is to act as an information resource for industrial and indoor environmental research by linking previous studies in these two fields. Particular attention is given to emission mechanisms and the influence of chemical, physical and environmental factors on such mechanisms. All three factors are significant to the emission process; for example residual VOCs will influence the glass transition temperature (Tg) of the semi-dry film depending on their composition and quantity, while test temperature will influence emission depending on its relation to Tg. Free vapour convection at the surface of a wet coating may cause surface air velocities similar to those observed indoors, suggesting no need for forced velocities in emission studies.

Key Words: volatile organic compounds, VOC, paint, coating, emission, drying, indoor air.

RÉSUMÉ

Ce rapport passe en revue la recherche effectuée sur l'émission de composés organiques volatils (COV) par les peintures et les enduits sur deux plans : (a) séchage et formation d'un feuil; (b) émissions de COV dans l'air intérieur. Le premier plan a fait l'objet de recherches par l'industrie de la peinture pendant des décennies, surtout dans le but de comprendre les mécanismes de séchage pour ainsi contribuer à la mise au point et à la formulation des produits. Le second a commencé à susciter l'intérêt plus récemment, les chercheurs voulant prédire et maîtriser l'effet des émissions de COV par les peintures et les enduits sur la qualité de l'air intérieur. Pour cela, il faut comprendre les mécanismes d'émission de COV, et la recherche dont il est ici question vise à examiner les résultats d'études menées sur le séchage de la peinture afin de les appliquer aux recherches actuelles effectuées sur les émissions de COV. L'objectif premier est de fournir de l'information aux chercheurs des secteurs de l'industrie et de l'environnement.

Cet examen a porté sur 120 ouvrages de référence clés publiés au cours des 30 dernières années. L'accent est mis sur les peintures au latex à base d'eau et les enduits à base de solvant traditionnels destinés aux bâtiments plutôt que sur les enduits industriels dernier cri produits ces dernières années. Le processus d'application et les mécanismes de séchage sont passés en revue pour chacun d'eux. On a également procédé à un examen partiel des constituants de la peinture volatile et des risques qu'ils posent pour la santé.

Les enduits à base de solvant forment des feuils semi-secs par évaporation limitée par la volatilité, à la façon d'un solvant pur, mais ce procédé est compliqué pour les produits à plusieurs solvants en raison des changements de composition et des interactions moléculaires. Le taux d'évaporation tombe rapidement à près de 50 % de la teneur en résine vol/vol à mesure que la diffusion devient cinétiquement limitante. Les enduits «durcis» peuvent renfermer 20 % de solvant vol/vol. Les volumes molaires de molécules de solvant sont alors cruciaux pour le processus d'évaporation et non pour la volatilité du solvant. Les coefficients de diffusion du solvant dans la résine, la concentration du solvant et la température de transition du verre du complexe résine-solvant sont d'importants paramètres pour l'évaporation limitée par la diffusion. Le séchage des peintures au latex à base d'eau est compliqué par le transport et la coalescence des particules de latex et par l'effet de l'humidité relative sur la perte volatile d'eau par rapport au solvant. Les peintures au latex sont formulées avec des solvants particuliers qui s'évaporent lentement afin de pouvoir aider les particules de latex à coalescer et à former un feuil continu, un processus qui peut prendre plusieurs jours. Par la suite, l'évaporation du solvant coalescent, limitée par la diffusion, est nécessaire pour former un feuil durable et peut être modifiée par la plastification de l'eau résiduelle, un effet que ne connaissent pas les enduits à base de solvant.

Les études sur les émissions de COV ont principalement porté sur la modélisation mathématique du processus d'émission et des effets d'absorption des surfaces intérieures des chambres expérimentales ou de l'intérieur des bâtiments. De nombreuses études n'ont porté que sur des feuils semi-secs et des études récentes, mais de portée limitée, ont évalué à la fois des feuils humides et semi-secs ainsi que des modèles empiriques appropriés pour les émissions de COV. Des prédictions théoriques ont été faites au sujet de la dynamique de l'émission limitée par la volatilité et par la diffusion, mais aucun de ces processus n'a fait l'objet d'une démonstration

expérimentale. La recherche sur l'émission limitée par la volatilité menée sur diverses sources humides a pu modéliser le comportement de sources ne formant pas de feuil (teinture, cire), mais pas le comportement tardif d'un enduit de polyuréthane, probablement parce que la diffusion devient le mécanisme prédominant.

Le rapport conclut en proposant des orientations en vue de recherches futures. La pertinence de la volatilité ou de la diffusion dans le processus d'émission et de sa dynamique doit être clarifiée, surtout lorsqu'il s'agit de choisir les bonnes conditions d'application (subjectile, épaisseur, ratio de charge, conditions environnementales) afin de simuler les conditions réelles. Le rôle de la vélocité de l'air par rapport au flux évaporatif des enduits humides doit être mieux compris. L'examen a été limité, mais la convection libre pour une surface en évaporation pourrait mieux simuler la vélocité de l'air sur une surface intérieure qu'une vélocité par air pulsé.

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1. INTRODUCTION

A wide range of paints and coatings are industrially produced, eg. corrosion-resistant paints, industrial coatings, automotive paints etc. However, this report focuses solely on interior paints and coatings which are used as decorative finishes within buildings. These will include pigmented coatings, lacquers and stains. Their common feature is that they are applied under available field conditions as liquid films which dry by loss of volatile constituents.

Coatings are complex products that use selected organic solvents to ensure a range of performances, such as:

(a) suitable liquid flow properties for easy application,
(b) an initial drying rate balanced to minimise further liquid flow while allowing levelling of the film,
(c) wetting of and adhesion to the substrate material,
(d) coalescence of the paint vehicle (resins) to ensure a continuous, protective film, and
(e) escape of residual solvents and additives to ensure a hard, durable film.

Water and organic solvents are critical to these processes, both while in the coating and while escaping from it. Accordingly, paint technologists and researchers have investigated the above processes for some decades in order to understand them and to develop optimised paint formulations. In contrast, volatile organic compound (VOC) emissions from coatings have been researched more recently in order to protect the ambient environment (by limits on VOC contents of paints) and to improve indoor air quality (by volatile emission rate limits during and after product application). While much of today's efforts to limit VOC contents of paints stems from the former concern, there is growing evidence that VOC emissions from paints can affect occupant health due to high indoor VOC concentrations at application and sustained concentrations after application (Gustafsson 1992, Rothweiler et al. 1993, Norback & Edling 1991).

It is believed that activities in the latter area of research – paint VOC emissions to indoor air – can benefit from previous paint drying and film formation studies carried out by the paint industry. This review will link these two areas of research in order to provide better direction to and interpretation of VOC emission studies. The primary aim of the review is to act as a resource guide for researchers in industrial and environmental fields. The author provides his own interpretation of a few areas of significance after presentation of the review.

2. METHOD OF REVIEW

The review considers published reports which were gathered by the following processes:

(a) a search of international databases:

– Chemical Abstracts	(1967–1995)
– NTIS	(1964–1996)
– Sci Search	(1974–1995)
– Enviroline	(1975–1995)

(b) direct contact with current researchers in the field and the paint industry, specifically:
  - * Maurizio De Bortoli, Indoor Pollution Unit, European Commission, Italy
  - * John C.S. Chang, Indoor Environment Management Branch, USEPA, North Carolina
  - * Per Axel Clausen, National Institute of Occupational Health, Denmark
  - * Al Hodgson, Staff Scientist, Lawrence Berkley Laboratories, California
  - * Bruce Leary, Research Manager, Dulux (Aust.) Pty Ltd, Australia
  - * Hans Gustafsson, Swedish National Testing and Research Institute, Sweden
  - * John C.Y. Shaw, Senior Researcher, Building Performance Laboratory, Institute for Research in Construction, NRC, Canada;

(c) manual searches of paint technology, polymer science and indoor air journals.

In total, approximately 120 references were gathered covering a period from the 1960s to 1996, and these form the basis of this review.

3. THE COATING PROCESS

A paint is a substance composed of solid colouring matter and film-forming resins intimately mixed with a volatile liquid vehicle and applied as a coating. A lacquer consists of a clear resin dissolved in a volatile solvent, sometimes with pigment added, and applied as a protective coating to wood or similar porous surfaces. A stain is a solution or suspension of colouring matter in water, solvent or oil designed to colour a surface (particularly wood) by penetration without hiding the surface. For the purpose of this review, all are classed as interior coatings.

3.1 Coating Constituents

Broadly, coatings consist of a mobile (liquid) phase and resins, fillers and other constituents. The mobile phase and specific constituents that escape from the coating will be focussed on here. Modern coatings are largely water-based latex paints or solvent-based resin solutions, while many of the new low-VOC coatings utilise novel coating technology which will be discussed separately (Section 7.1).

3.1.1 Water-based paints

Water is a poor solvent for organic resins and so water-based paints are generally water-reducible resins (where the resin is dissolved in an alcohol and then diluted with water) or more commonly polymer latexes. Water soluble resin coatings consist of an acidic or basic polymer, an auxiliary solvent, a neutralizing agent and water. Auxiliary solvents include n-butanol, 2-butanol, butyl glycol and propylene glycol ethers. Ammonia, amines and amine derivatives are used as neutralising agents (eg. triethylamine, dimethylethanolamine, dimethylaminomethylpropanol). Auxiliary solvents and neutralizing agents are important for resin solubility but will be emitted during the drying process (Doren et al. 1994). Water-based latexes are more commonly used in decorative coatings and include a range of organic solvents to ensure:

(a) good solubility and stability of the resin,

(b) controlled rate of drying,

(c) absence of composition changes during drying that can cause precipitation of the resin,

(d) coalescence of latex particles during drying to ensure formation of a continuous film, and

(e) escape of solvent residues to reduce film softness.

A range of cosolvents is needed to provide these properties and typical solvents include methylethylketone (MEK), isopropanol, propoxypropanol, butoxyethanol and ethoxyethoxy-ethanol. Typical VOC contents are approximately 180 g/L. Generally (d) and (e) require the use of a "coalescing solvent" located in the latex particles. For latex particles to coalesce, the glass transition temperature[•] (Tg) of the constituent polymer has to be below the ambient temperature but this means the polymer film will be soft and retain dirt. The presence of coalescing solvent reduces the "effective" Tg (at application) of high Tg latex particles. The coalescent solvent later slowly evaporates resulting in a paint film with a Tg well above ambient temperature (Wicks et al. 1992).

[•] the glass transition temperature of a polymer is the temperature above which the long-chain polymer molecule or segments of the molecule attain molecular mobility.

Other main constituents of interior latex paints are:

* ethylene glycol and propylene glycol as "lapping"[*] and anti-freeze agents,
* surfactants to stabilise the pigment dispersion and latex,
* titanium dioxide – white pigment; zinc oxide – pigment and effective fungicide,
* attapulgite clay to impart flow properties (shear thinning, thixotropy),
* supplemental fungicides – includes aromatic mercury compounds (eg. phenylmercuri-acetate) although these are prohibited in some countries such as the US; note that Tichenor et al. (1991a) demonstrated mercury emission from paints using environmental chamber experiments,
* latex resins of polyvinyl acetate (Tg 32°C) or its copolymers (eg. butyl acrylate copolymer) – generally present at a volume content of approximately 37%.

3.1.2 Solvent–based coatings

Solvent–based coatings are typically solution systems such as alkyd enamel paints and polyurethane lacquers. Blends of up to ten solvents can be used, selected to ensure resins dissolve and stay dissolved during drying as well as to control the rate of drying. VOC contents above 275 g/L are generally used.

The organic solvents used in coatings can be classified into three broad categories:

(a) weakly hydrogen-bonding
  - aliphatic and alicyclic hydrocarbons eg. naphthas provide high volatility for lacquers, mineral spirits for slower evaporation and as replacement for turpentine from trees,
  - aromatic hydrocarbons dissolve a broader range of resins eg. toluene and xylene are used on a large scale,
  - chlorinated hydrocarbons (use increasingly limited due to toxicity).

(b) hydrogen bond acceptors
  - ketones and esters eg. ethyl-, isopropyl- and butyl acetates, and MEK, methylisobutylketone (MIBK) and methyl-n-amylketone (MAK) are the most widely used (Wicks et al. 1992b). Slow evaporating esters are 1-methoxy-2-propyl acetate and 2-butoxyethylacetate.

(c) hydrogen bond donor-acceptor (alcohols)
  - most widely used are methyl-, ethyl-, isopropyl-, n-butyl-, sec-butyl- and isobutyl alcohols.

Within these broad categories the general rule of "like dissolves like" is broadened. A mixture of weak H-bonding hydrocarbon with strong H-bonding alcohols gives similar solvency to medium H-bonding esters and ketones. However paint solubility properties with mixed solvents are complex and not fully understood (Wicks et al. 1992b).

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[*] "lapping" is the process during application where paint can be applied to a film applied shortly before, without damage to the partially-dried film.

3.1.3 Toxicity of paint constituents

Information on this subject can be gathered from three areas:

(a) specific health hazard (i.e. potential for harm) information for individual constituents,

(b) health risk (i.e. likelihood of hazard occurring) information for constituents during paint manufacturing processes, and

(c) health risk information for constituents during and after paint application.

A brief overview of these areas is provided for perspective to this report.

3.1.3.1 health hazards of constituents

These have been summarised in several reports (Hansen et al. 1987, Holmes 1991, Murdoch et al. 1996) as follows:

* solvents – most organic solvents are central nervous system depressants and at high acute exposures cause transient effects of headache, drowsiness and fatigue; chronic exposure at levels exceeding occupational exposure standards also cause disturbances in memory and concentration, depression and irritability; there is some debate over the effect of chronic exposure of painters and irreversible brain and nervous system damage (see Section 3.1.3.3); solvents may be odorous and contribute to nervous membrane and respiratory tract irritation (particularly butanol and the ketones and esters); most solvents are toxic to the liver to some degree, especially chlorinated solvents, and there is some evidence of an association between moderate exposure to hydrocarbons and kidney disease; some solvents present reproductive hazards, e.g. ethers of ethylene glycol; some solvents have been classified (IARC) as cancer-causing agents, e.g. benzene, tetrachloroethylene, carbon tetrachloride, styrene, dichloromethane.

* other gases and vapours – amines (neutralising agents) may be odorous and contribute to mucosal irritation, e.g. ammonia and triethylamine are respiratory tract, skin and eye irritants; triethylamine is a sensitiser; formaldehyde (as a biocide) is a respiratory tract, skin and eye irritant, a skin sensitiser, a possible cause of occupational asthma and an animal carcinogen (nasal cancer) at high levels; diisocyanates (from polyurethane lacquers) are severe irritants to eyes, skin and respiratory tract and may cause respiratory sensitisation and subsequent susceptibility to asthma; residual monomers in acrylic latex resins (e.g. methyl methacrylate and butyl methacrylate) are odorous and respiratory tract, skin and eye irritants and some (e.g. butyl acrylate and 2-ethyl hexyl acrylate) are skin sensitisers even at low levels.

* biocides – most are skin sensitisers.

* surfactants – may contribute to skin irritation or act as sensitisers.

* driers (to accelerate latex curing) – salts of cobalt or zirconium may sensitise.

3.1.3.2 health risks during paint manufacture

The National Paint and Coatings Association (1993) summarised findings of a study of 187 US workers from paint manufacturing plants who were exposed to chronic, low levels of mixed organic solvents. The study focussed on "toxic brain syndrone", identified in earlier Scandanavian studies where exposures were probably very high (but poorly characterised) and confounding factors were not accounted for. All workers were found to perform within the clinical "norms" of a range of neuropsychological tests. However, subtle, dose-related neurobehavioural effects for both central and peripheral nervous systems were demonstrated (e.g. sense of smell), but were not considered of clinical significance.

Murdoch et al. (1996) evaluated solvent exposure and health effects for 153 workers at seven Australian paint manufacturing workplaces, selected to represent a cross-section of the industry. Ninety-seven percent of all personal air samples were below the "hygienic effect" exposure standard of 1.00 (standardised additive solvent exposure) and 60% were in the range 0-0.2. No particular solvent dominated the exposures. Respiratory testing found that potentially exposed and miscellaneous workers had a 5-10% reduction in lung function c.f. laboratory and clerical workers, the effect possibly being reversible and due to airway irritation from gascs, vapours and dust, (even though exposure to these occurred at levels below occupational exposure standards). Small effects or neurobehavioural function were also found in workers exposed to solvents, e.g. tiredness, painful tingling sensations, memory effects and decision speed. It was concluded that compliance with current exposure standards may not protect against health effects which were not considered when the standards were established.

3.1.3.3 health risks during and after painting

Holmes (1991) summarised general findings on the occupational health of painters from research commissioned by the USA Painters' Union. Apart from skin diseases, lung diseases included lung irritation (a continuum of respiratory symptoms from acute lung irritation to chronic bronchitis which were probably due to a range of causal agents including VOCs) and occupational asthma. Some paint components were identified as potential reproductive hazards. Recent reports on occupational cancer risks had shown no increased risks in the paint manufacturing industry, but consistent and significant increased risks to painters for cancers of all sites and lung and bladder cancer. The International Agency for Research on Cancer (IARC 1989) concluded that occupational exposure as a painter should be classified as carcinogenic (Group 1). Specific causative agents were not identified but known carcinogens in paints include some VOCs (benzene, dichloromethane, carbon tetrachloride, tetrachloroethylene, epichlorhydrin, toluene diisocyanate), pigments, fillers and dyes.

Most organic solvents at high exposure act as acute suppressants of the central nervous system, as discussed earlier (Section 3.1.3.1). Prolonged, high exposure of painters to solvents has been reported in clinical studies, mainly in Scandinavian countries, to lead to mild to severe neurobehavioural dysfunction or psychiatric disorders. Such clinical reports have not appeared elsewhere in the world and have been subject to criticism, but it is probable that spray application of interior paints in these countries in the past led to massive solvent exposures. A review of typical occupational exposures to VOCs in painting, printing and adhesives observed that permanent chronic effects may be occurring, including neurobehavioural effects, neurophysiological effects (such as electroencephalogram and electromyogram changes) and alterations in sensory thresholds (Brown et al. 1992).

Trials with roller application of a solvent-borne paint showed that occupational exposure standards (in region of 500 mg/m^3 for hydrocarbons) were exceeded 20-30 minutes into the painting operation even with high ventilation rates of 7-11 air changes per hour (Dearling et al. 1992). Trials with water-based paints found that while occupational exposure standards for constituents were not exceeded, health effects such mucosal irritation and headache occurred, probably due to a combined action of ammonia, formaldehyde and solvents (Hansen et al. 1987).

VOC concentrations in the indoor air of new buildings may take periods of weeks to months after construction to diminish to "background" levels (Brown et al. 1992) and interior paints and coatings are expected to be one of the contributors to this pollution. Norback et al. (1996) reported that the prevalence of weekly symptoms (compatible with the sick building syndrome) in a sample of the general Swedish population was significantly related to exposure to indoor surfaces painted in the previous year for females and for subjects with atopy. In particular it was suggested that irritation of the eyes, nose, throat and facial skin were caused, especially from exposure to wood paints. Pollutant measurements in 62 of the dwellings showed that formaldehyde, aliphatic compounds (C_8 – C_{11}), butanols and TXIB (2,2,4-trimethyl-1,3-pentanediol diisobutyrate) were significantly elevated in the dwellings that were newly painted.

3.2 Application Methods

Coatings are applied by a range of application methods, eg. brush, roller or spray, and often as a combination of layers, eg. primer, undercoat and topcoat when coating timber skirting and architrave with enamel paints. In many interior applications only a sealer and topcoat or topcoat alone are required, eg. painting of gypsumboard and fibre-cement, respectively. Coating thickness can vary from the 50–70 μm wet film thickness for general applications to several hundred μm for special applications.

All of these factors will influence paint drying properties and VOC emissions and will be described where appropriate in the review.

3.3 Observed Drying Behaviours

Evaporation is the process by which a material (or part of it) is converted into a gas or vapour state. Drying of coatings is considered to be the combination of processes by which volatile matter evaporates from an initially liquid film to produce an end product with desired physical properties. Thus evaporation refers not only to volatile loss from the liquid film but also from the semi-dry film.

3.3.1 Solvent–based coatings

Solvents for coatings are selected so that initially they escape relatively quickly to prevent excessive flow, but sufficiently slowly to provide levelling and adhesion. The first 30% of solvent evaporates from typical alkyd coatings as quickly as the neat solvent, essentially at a constant rate depending on volatility. Later-stage solvent evaporation occurs several times more slowly and is rate-controlled by solvent diffusion to the surface of the coating. The transition point between these behaviours has been defined as the resin solids content at which the evaporation rate due to volatility equals that due to diffusion, eg. as shown in Figure 1 (Ellis 1983).

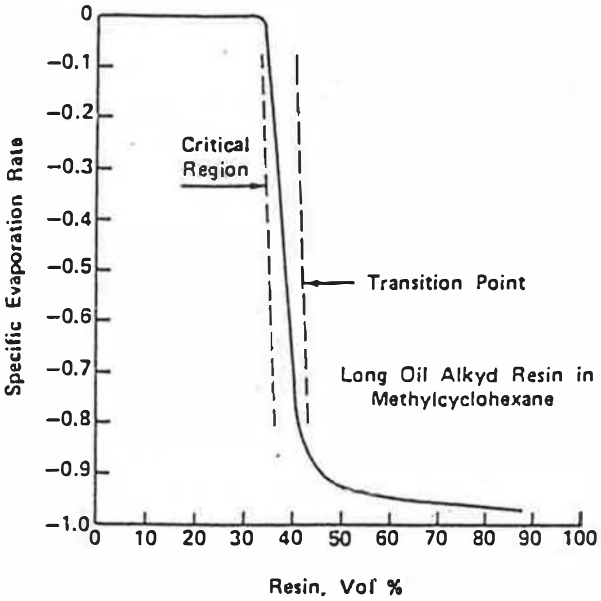

Figure 1. Transition from volatility–limited to diffusion–limited evaporation, as shown by specific evaporation rate (Ellis 1983).

Transition points have been observed to typically occur at resin solids contents of 40–50% by volume. This means that alkyd coatings, normally formulated at 27–40% resin solids, generally exhibit rapid initial solvent release which is volatility-limited. However high solids coatings are usually formulated at 65–75% resin solids and solvent evaporation through the whole drying process is diffusion-controlled and solvent volatility cannot be used to control initial setting.

3.3.2 Water–based latex paints

3.3.2.1 drying of water component

Vanderhoff et al (1973) found that water evaporated from a latex film in 3 stages:

(a) an initial constant evaporation-rate stage during which the latex particles moved freely,

(b) an intermediate stage when the latex particles came into irreversible contact and water evaporation rate dropped rapidly to 5–10% of initial rate; this stage was complete when virtually all the water had evaporated and a nascent resin film had formed; and

(c) a final stage when water escaped the film very slowly by diffusion; the dry film later underwent gradual coalescence and became increasingly homogeneous by diffusion of polymer chain ends across the inter-particle boundaries (see Section 3.4.2).

More recent studies have provided further details:

Stage (a): Silvartoinen (1985) observed that the initial evaporation of water occurred at the same rate as water alone. Croll (1985) observed that coatings lost water at 85–90% the rate of water alone as a result of greater surface cooling due to restriction of convective heat transfer into high viscosity films; otherwise, the drying resembled water evaporation and was controlled by temperature, humidity, evaporative cooling and surface air flow.

Stage (b): Silvartoinen (1985) observed the transition to stage (b) occurred at approximately 30% w/w water (depending on pigment volume content and film thickness) and proposed that moisture movement then occurred by capillary flow. Croll (1987) proposed that initial drying occurred at a constant rate through a "dry" porous surface layer supplied by a wet transition layer between the surface layer and the latex. Drying rate slowed sharply after the transition layer reached the substrate (Figure 2) and the reservoir of water for evaporation became increasingly depleted. Stage (b) was considered to start later in thicker films because the transition layer had further to go to reach the substrate.

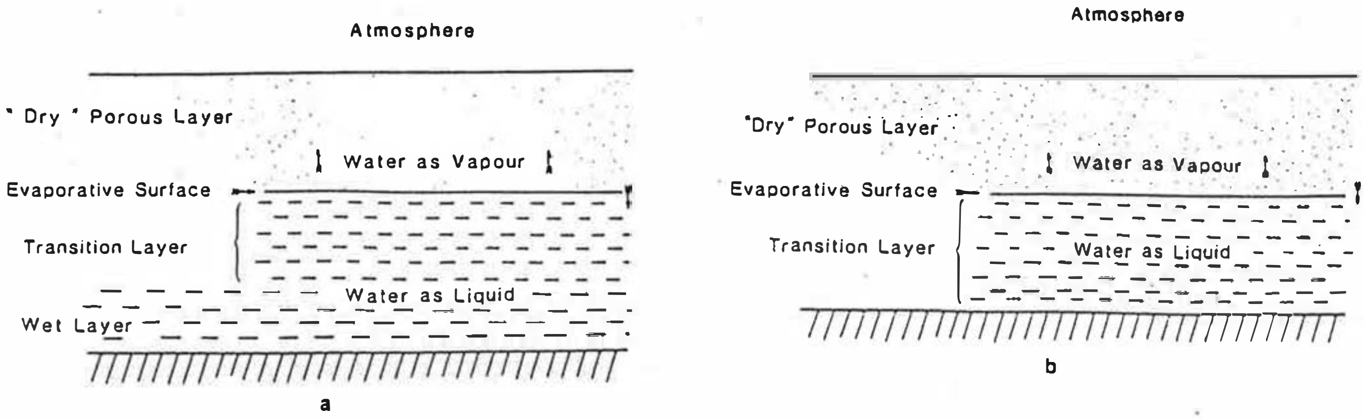

Figure 2. (a) coating structure during the constant rate period.
(b) coating structure at the start of the falling rate stage (Croll 1987).

Stage (c): Silvartoinen (1985) observed this stage occurred at approximately 10% w/w water content depending on the pigment volume content. Sullivan (1975) observed that water loss in this stage was identical for different film thicknesses when measured according to a reduced time variable, time/(thickness)^2, indicating drying was controlled by internal diffusion resistance.

3.3.2.2 drying of solvent components

Solvent evaporation from waterborne latex coatings exhibits greater complexity. Sullivan (1975) observed that water-solvent interactions and partitioning of solvents between latex particles and water led to complex water loss behaviour. He found that the evaporation rates for solvent up to periods of 5 hours were in the order of their volatilities. However at longer times, the low volatility ethylene glycol had the fastest evaporation rate since it partitioned to continuous hydrophilic interstices between latex particles from which its evaporation was controlled by volatility. Other solvents, notably the coalescents, partitioned to the resin phase from which their evaporation rates were diffusion-controlled.

Hansen (1974) observed identical cosolvent and coalescent solvent evaporation rates for a coating at different thicknesses when plotted using the reduced time variable (time/thickness). He concluded that volatile organic losses from latex coatings were controlled by surface evaporation processes. Note however that this differs from findings for late-stage solvent evaporation from solvent-based coatings (see Section 4.3) and the observations of Sullivan (1975) for stage (c) water evaporation from latex coatings.

The early drying behaviours of solvent components from a water-based latex coating are critical to the development of an acceptable film. Organic cosolvents may be added to speed up the drying process but rapid solvent loss may lead to polymer precipitation in cosolvent-depleted water. The relative humidity during application is a critical factor to solvent evaporation from these coatings. At high humidities water evaporation will be inhibited and the cosolvent will escape leading to a water-rich coating. At low humidities water evaporation will be enhanced and a cosolvent-rich coating will remain. An approach adopted to deal with this problem has been to select water-solvent azeotropes – mixtures where the liquid and equilibrium vapour have the same compositions. In practice azeotropy functions only in dry air and so cosolvents are selected appropriate to relative humidity conditions at application (Rocklin et al. 1986). For each cosolvent, there exists a critical relative humidity(CRH) for azeotropy to occur (depending on cosolvent concentration and air speed). For example CRHs at 20 volume per cent cosolvents are (Eaton and Willeboordse 1980):

Group 1:	methylethylketone, isopropanol	0%
Group 2:	propoxypropanol	25%
	butoxyethanol	74%
Group 3:	ethoxyethoxyethanol	93%

Under conditions expected indoors, Group 1 cosolvents flash off quickly to leave a water-rich tail while Group 3 remain as “tail” solvents to function as coalescing aids.

It has been found that CRHs are different in coatings than in water-cosolvent blends, possibly due to cosolvent distribution between water and latex particles (Wicks et al. 1992a).

3.4 Film Formation

Film formation from coatings may involve chemical reactions (polymerisation, cross-linking), but these will not be considered in this review. Only processes associated with the evaporation of volatiles to provide the final film will be discussed.

3.4.1 Solvent-based coatings

The main complication in film formation from resin solutions is the residual strain that is created in the dry film as a result of solvent loss after the coating has solidified (Croll 1979, 1979a). After solidification, coatings tend to shrink as they lose residual solvent. However since they are bonded to rigid substrates, residual strains are induced in the dry films. Croll showed that:

(a) coatings “solidified” at the point when the glass transition temperature Tg of the polymer-solvent mixture coincided with ambient temperature (e.g. for three different polymers with toluene this point occurred at 16–22% v/v solvent);

(b) the residual strain level was dependent on the quantity of solvent that was lost after solidification had occurred (high residual strain could cause loss of coating-substrate adhesion).

3.4.2 Water-based latex paints

After much of the water has evaporated from these coatings, the polymer latex particles must deform and flow to form a continuous film. The viscoelastic character of the latex particle will be the main feature determining film formation. However, since soft, deformable polymers will not provide useful coatings it is common to use hard, semi-rigid polymers to which specific coalescing solvents (or filming aids) have been added. It is intended that these solvents evaporate after the coating has formed a continuous film so that a hard, durable product results. Selection of coalescing solvents is made according to three factors (Hoy 1973):

(a) their distribution between the aqueous and polymer phases during film formation. Solvents with high hydrogen bonding are found mainly in the aqueous phase while those with moderate hydrogen bonding will localise in latex particles. For the former, the absorption behaviour of porous substrates and the relocation of solvent to latex particles during drying will be critical to the film forming process.

(b) their plasticising efficiency for the polymer. Minimum filming temperatures (MFT) exist for latex coatings. These are the minimum application temperatures at which latex particles will coalesce and form a film during drying; at lower temperatures evaporation of water results only in a powdery finish having no cohesion. Hoy showed that MFT could be calculated from the volume fraction of the coalescing aid V_a and the glass transition temperatures (degrees Kelvin) of the polymer and coalescing aid, Tg_p and Tg_a respectively, by:

$$\frac{1}{MFT} = V_a \left[\frac{\alpha Tg_p - Tg_a}{K.Tg_p.Tg_a} \right] + \frac{1}{K.Tg_p} \qquad (1)$$

where

$K = \frac{MFT}{Tg}$ is the reduced filming temperature for the system (and is typically 0.92–0.98),

$\alpha =$ factor accounting for mobility of coalescent solvent external to the latex particle; and lastly

(c) their ability to evaporate from the coating after completion of film formation.

Nicholson (1989) noted that the mechanism of latex coalescence was not completely understood but that it probably involved surface tension and capillary attraction factors, the viscoelastic nature of the latex polymer and relocation of surfactants away from polymer surfaces, a process described by Vanderhoff et al (1973). Eckersley and Radin (1994) proposed a comprehensive model of film formation based on these factors. As predicted by the model, they showed that small radius particles fused more completely at room temperature. Nicholson noted that internal stresses (and resulting film faults) also developed in latex paint films as they dried but were prevented by optimum levels of coalescing solvents (such as Texanol® (2,2,4-trimethyl-1,3-pentanediol monobutyrate)).

Mazur and Plazek (1994) focussed on the physical processes occurring when latex particles come into contact. They defined two stages of the coalescence process:

(a) neck growth – formation of an interface between latex particles by flow and/or deformation of contacting particles, and

(b) equilibration – evolution of bulk properties via chain diffusion and stress relaxation in the vicinity of the interface.

Early stages of neck growth for polymers above Tg were found to occur by quasi-elastic (recoverable) deformation of the contacting surfaces. Neck growth occurred over periods of hours to days. Qualitative observations showed equilibration required comparably long times of the order of the terminal relaxation time of the polymer (~ tens of hours, depending on temperature). Vanderhoff et al (1973) observed that complete coalescence of latex particles of many resins required several days to occur at room temperature.

Keddie et al (1995) investigated the kinetics of film formation by a range of acrylic latexes. They observed that onset of film formation occurred when particles gained close contact by loss of water and particle deformation and that this occurred at the same normalized time, regardless of Tg of the latex. This was the time when there was less than 15 volume per cent of water in the latex. Later stages of film formation – particle deformation and packing, coalescence to a homogeneous material – were dependent on Tg.

4. DRYING MECHANISMS FOR SOLVENT–BASED COATINGS

It is generally regarded that there are two barriers to solvent evaporation from a polymer solution:

(a) the resistance to solvent loss at the air-liquid interface, and

(b) the resistance to transport of solvent by diffusion within the coating to the air interface.

(a) is essentially the volatility-limited process that occurs early in the drying process and is affected by the vapor pressure of the solvent, its latent heat of vaporization and solvent transport via the air boundary layer at the coating surface. (b) occurs later in the drying process (eg. once the coating is touch dry) and is dependent on the solvent's diffusion coefficient in the film; this is a very slow process that is important since the residual solvent acts as a strong plasticizer (relieving film stress) and may remain in the polymer film for years. A transition process will occur as drying shifts from mechanism (a) to mechanism (b) (Hansen 1970).

These mechanisms and the period of the drying process to which they apply will influence solvent emission dynamics from coatings and will be reviewed from this perspective.

4.1 Volatility–Limited Period

Since the initial evaporation rates for many coatings are similar to the evaporation rates exhibited by neat solvents, the evaporation mechanisms for solvents and solvent mixtures will be reviewed first.

4.1.1 Single solvents

Single solvents evaporate at constant rates depending on their volatilities and the physical conditions of the method of measurement. For any particular method, evaporation rates are generally proportional to solvent vapour pressure, as shown in Table 1.

Table 1. Solvent vapour pressure at 25°C and time to 90% evaporation in the Chevron Research Evapocorder(Ellis 1983)

Solvent	Vapor Pressure (torr)	t_{90} (min)	Solvent	Vapor Pressure (torr)	t_{90} (min)
Isooctane	49	6.7	Ethylbenzene	10	27
n-Heptane	47	8.0	p-Xylene	9	31
Methylcyclohexane	47	8.0	n-Butylalcohol	6	51
Toluene	32	12	Cumene	5	49
Isobutylacetate	20	25	n-Nonane	5	51
2,2,5-Trimethylhexane	17	16	n-Propylbenzene	2	65
n-Octane	15	20	2-Ethoxyethanol acetate	2	100
Ethylcyclohexane	13	20	1,2,4-Trimethylbenzene	1	99
n-Butylacetate	13	34	n-Decane	<1	129
Isobutylalcohol	13	36			

The Shell Thin-Film Evaporometer (ASTM 1995) is an industry standard method for comparing the evaporation rates of volatile solvents. The method determines the time to 90% evaporation of a solvent applied to blotting paper under well-defined physical conditions. The relative evaporation rate (R_e) to that of n-butyl acetate is then determined and can be a useful guide for comparison of solvent systems under other conditions. This data is presented in Appendix B for a range of typical solvents.

Two classical theories have been proposed for solvent evaporation: Langmuir-Knudsen theory (Reynolds 1963) and Gardner's theory (Yoshida 1972). The former considered that for a closed system with equilibrium between the solvent and vapour, the number of molecules evaporating from the surface equals the number condensing and showed:

$$W_S' = p_i^o M^{1/2} \left(\frac{f^2}{2\pi RT} \right)^{1/2} \tag{2}$$

where W_S' = evaporative flux rate of solvent (mass/area.time)
p_i^o = vapour pressure of pure solvent i at temperature T
M = molecular weight of solvent molecules
f = condensation coefficient (ratio of molecules condensing to molecules arriving at liquid surface).

In contradistinction, Gardner proposed that vapour diffusion through a boundary layer at the liquid surface was the rate determining step of evaporation and showed

$$W_S' = \frac{k_d}{RTP\delta} dM p_i^o = k' dM p_i^o \tag{3}$$

where k_d = vapour diffusion rate constant
P = external pressure
d = diffusion constant of the vapour boundary layer
δ = boundary layer thickness.

Yoshida (1972) noted that both equations had been found to agree well with evaporation of petroleum hydrocarbons. He described the measurement of evaporation rates with the Shell Automatic Thin Film Evaporometer at different air velocities (v). Most solvents exhibited linear relationships between W_S' and v (evaluated in the range 0.2–1.7 m/sec). Exceptions were solvents with high heats of vaporation or fast evaporation rates since these exhibited depression of surfaces temperatures at high air velocities, which in turn depressed evaporation rates. Consistent with the above equations, log (W' /v) was linearly related to log (p_i^o M) for many solvents. f in equation (2) was of the order of 10^{-5} to 10^{-4} and (k'd) in equation (3) was approximately 10^{-6} and both were independent of the type of solvent but were linearly related to v.

Stratta et al (1978) expressed Gardner's equation (differently) as:

$$W_S' = k_v T^{1/2} p_i^o \tag{4}$$

where k_v = vapour diffusion mass transfer coefficient at any velocity v.

The air velocity dependence of k_v in the region 0 to 0.5 m/sec was found to be

$$k_v = k_o + \frac{v}{Av + B} \tag{5}$$

where A and B were wind speed coefficients for the mass transfer coefficient.

They found the following empirical relationship for the evaporative flux:

$$W' = 1.86 + \frac{v}{0.0155v + 0.0706} \tag{6}$$

They also found these same empirical constants could be used with Relative Evaporation Rate (R_e) data for other solvents (x) to estimate their evaporative fluxes at different air velocities:

$$W_x' = \frac{R_{e,x}}{R_{e,nba}} \left(1.86 + \frac{v}{0.0155v + 0.0706}\right) \tag{7}$$

Note that this relationship applied to the particular experimental conditions evaluated and that other conditions, particularly air turbulence, would significantly alter it.

4.1.2 Solvent mixtures

In the ideal case of solvent mixtures, Raoult's law predicts that the vapour pressure p_i of component i is reduced from the vapour pressure p_i^o of pure i in proportion to its mole fraction x_i:

$$p_i = x_i p_i^o \tag{8}$$

For molecules of similar molecular weights and liquid diffusion constants, the rate of evaporation is proportional to p_i and so:

$$\frac{dc_i}{dt} = x_i W_i^{o\prime} \tag{9}$$

where c_i = vapour concentration of component i.

Note that since different solvents have different vapour pressures and evaporation rates, the composition of the solvent vapour will be different from that of the liquid and so the liquid composition will change continuously as evaporation progresses. For two components, a and b, exhibiting vapour concentrations, c_a and c_b, respectively:

$$\frac{dc_a}{dc_b} = \frac{W_a^{o\prime} x_a}{W_b^{o\prime} x_b} = R_{ab}\frac{x_a}{x_b} \approx R_{ab}\frac{c_a}{c_b} \qquad (10)$$

$$\log c_a = R_{ab} \log c_b + (\log c_{ao} - R_{ab} \log c_{bo}) \qquad (11)$$

Thus log c_a should exhibit a linear relation to log c_b with a slope equal to the relative evaporation rates of the pure solvents (R_{ab}). Yoshida (1972) noted that this behaviour was exhibited by mixtures of weak H-bonding solvents but not by mixtures of weak H-bonding solvents with H-bonding solvents (eg. toluene-ethanol) since associations between H bonding molecules in the latter mixture were reduced relative to those in pure solvent. He included an empirical coefficient of activity γ ("escaping coefficient") to compensate for interactions, as follows:

$$W'_{mix} = \gamma_1 x_1 W_1^{o\prime} + \gamma_2 x_2 W_2^{o\prime} + \ldots \qquad (12)$$

The weight percentage of component i in the evaporating vapour was:

$$w_i = \frac{W'_i}{W'_{mix}} = \frac{\gamma_i x_i W_i^{o\prime}}{W'_{mix}} \qquad (13)$$

and so

$$\gamma_i = \frac{w_i W'_{mix}}{x_i W_i^{o\prime}} \qquad (14)$$

It is clear that the escaping coefficient will also vary continuously during evaporation due to compositional changes in liquid and vapour mixtures. Yoshida produced complex empirical activity coefficient curves for mixtures of different solvent types. Wicks (1992a) noted that computer calculations using such coefficients could estimate the approximate vapour pressures of solvent components throughout evaporation of a mixture but only for simple situations. The ability to accurately predict the evaporation process of complex solvent mixtures does not exist.

Evaporation of water-solvent mixtures involves further complications to solvent mixtures (Wicks et al. 1992a):

(a) strong interactions often cause substantial deviations from Raoult's law,

(b) relative humidity will strongly influence the evaporation of water but have little effect on the evaporation of solvents (discussed in Section 3.3.2.2), and

(c) azeotropic behaviour is particularly likely to occur and may be sought by formulators (discussed in Section 3.3.2.2).

4.1.3 Solvent-based coatings

The process of solvent evaporation from a resin solution has been divided into several steps as presented in Figure 3 (Sletmoe 1966).

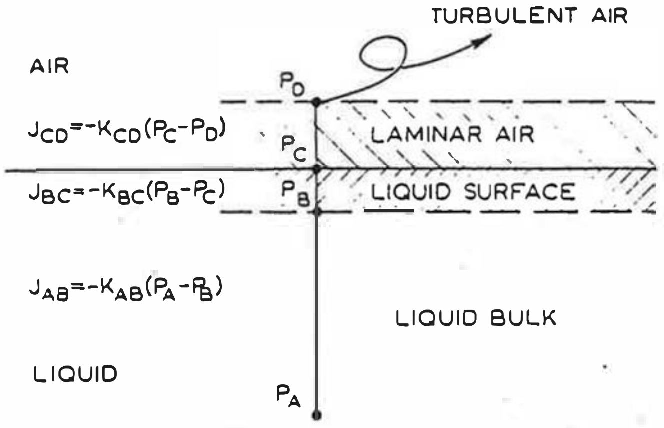

Figure 3. Steps involved in solvent evaporation from a resin solution (Sletmoe 1966).

Solvent molecules must diffuse (a) through the bulk liquid (A to B), (b) through the liquid surface film (B to C), and (c) through a stagnant air film adjacent to the liquid surface (C to D). Once the turbulent air region (D) is reached, the solvent molecules are rapidly swept away. Each of these steps may be limiting at different stages of solvent loss from paint films.

Many investigators have found that initial solvent loss rates from paints are similar for those for solvent alone, indicating surface evaporation to be the dominant, rate-limiting step. However solvent loss from the paint becomes slower as drying progresses and liquid film viscosity increases. For alkyd paints, this has been observed after 60% (Reynolds 1963) or as much as 80–90% of the solvent (Sletmoe 1966) has evaporated, solvent diffusion through the film then becoming the limiting factor. Raoult's Law (see Section 4.1.2) states that for an ideal system, the partial pressure of the solvent is reduced by the mole fraction of the resin solute. However due to the high molecular weights of resins, an effect is minimal and the partial pressure of solvent in the early evaporation phase of paints is similar to that of the neat solvent. Ellis (1983) demonstrated this by showing that the evaporation time for the first 30% by weight of solvent was generally the same for long oil alkyd resin solutions in a range of solvents as for the neat solvents. As discussed earlier (Section 3.3.1), the transition from volatility-limited to diffusion-limited processes can occur at 40–50% by volume resin content. Since alkyd coatings are normally formulated at 27–40% resin solids, departure from neat solvent evaporation rates are likely soon after the first 30% loss of solvent.

Yoshida (1972) described an equation by Chesunov and Vasenin for the rate of evaporation from coatings in the "constant rate period":

$$W_S' = c_b \, k_L \, v \left[1 - \exp\left(-\left(\frac{\Sigma^2 dL}{v}\right)\right)\right] \quad (1 - bt) \qquad (15)$$

where

c_b = concentration of vapor in the boundary layer
k_L = dimensionless shape factor of evaporating space
d = diffusion coefficient of solvent vapor
Σ = aerodynamic coefficient of molecular displacement
L = length of evaporating surface in direction of air flow
b = empirical parameter
v = air velocity

Feigley et al (1981) expressed the initial "wet surface" volatilization as:

$$W'_A = k_c(c_i - c) \tag{16}$$

where W'_A = surface flux of volatile species A (in g-moles/area.time)
c_i, c = gas phase concentrations of A at the air coating interface and in the bulk of the gas
k_c = mass transfer coefficient (cm/sec)

k_c was dependent on surface geometry and the air flow over the surface as well as the transport properties of A in the gas phase. Correlation equations have been developed for a number of surface shapes expressing k_c as a function of surface size, volatile diffusivity (d), the Reynolds number (Re) and the Schmidt number (Sc). The average mass transfer coefficient over the length (L) of a flat plate with a developing laminar boundary layer was estimated from:

$$k_c(\text{ave}) = 0.664\frac{d}{L}(\text{Re}_L)^{1/2}(\text{Sc})^{1/3} \tag{17}$$

Feigley et al evaluated the short term (<40 minutes), wet phase drying of a shellac solvent system (approximately 30% resin in predominantly ethanol and isopropanol). They used the above equations to predict the theoretical fluxes for ethanol and isopropanol from a neat solvent mixture but found these levels were approached only during the first three minutes of drying. As expected, they were not affected by coating thickness. Thereafter solvent emission rate steadily declined until approximately 90% of solvent had escaped, when the emission rate suddenly dropped. Mechanisms for these declines were not evaluated.

Blandin et al. (1987a) found that the rate of solvent evaporation from a coating varied with temperature in proportion to the vapour pressure of the solvent, yielding an empirical relation:

$$W' = \alpha\exp(-\beta/RT) \tag{18}$$

where α and β were empirical constants.

4.2 Transition Period

This period has been less studied than the evaporation- and diffusion-limited periods but Hansen (1970) noted that many of the anomolies of solvent loss can be traced to transition factors, particularly the volatile solvent content (C_t) of the film when this period is reached. For example:

(a) C_t is related to the amount of solvent required to reduce the glass transition temperature (Tg) of the film from that of the resin to the film temperature. Thus if the (solvent-free) resin Tg is below the film temperature, then no clear, prolonged diffusion-limited phase is expected. This is the case for many long oil alkyds.

(b) conversely to (a), polymers with high Tg values would enter the transition phase with high C_t values and overall solvent loss will be a slower process.

(c) excessive supercooling of the film (due to high heat of vaporization or high surface air velocities) will cause the transition phase to be entered at higher C_t values and overall solvent loss will be slower.

(d) other plasticising (small) molecules will reduce the Tg of the resin-solvent film and consequently C_t will be lower and overall solvent loss will be quicker, eg water and methanol are the most efficient plasticizers on a volume basis.

Yoshida (1972) noted that since wet film thickness became smaller as drying proceeded, the ratio of evaporating surface to film thickness became larger, and allowed for this in the equation

$$\log_e \left(\frac{C_o}{1 - C_o} \right) \left(\frac{1 - C_t}{C_t} \right) = k_d \frac{A}{v_r} t \qquad (19)$$

where C_o is the initial concentration of solvent in the film by weight, C_t is solvent concentration at time t, A the area of evaporating surface and v_r the volume of resin. When he plotted the left-hand side of this equation against drying time for an alkyd resin in xylene, he found the equation was only valid in the transition phase. He also observed that the duration of this transition (as judged by linearity of plotted results) decreased considerably (e.g. from 100 minutes to several minutes) when the surface air velocity increased from 0.3 to 1.7 m/sec. Explanations for these effects were not provided.

Ellis (1983) defined the transition point between volatility- and diffusion-limited evaporation phases as the resin solids content at which these phases exhibited equal evaporation rates (Figure 1). He observed that:

(a) transition points for a long oil alkyd resin occurred at higher resin contents for lower volatility solvents eg. iso-octane 36% by volume resin, toluene 40%, ethylbenzene 45%, p-xylene 49%, 1,2,4-trimethylbenzene 55%, n-decane 55%;

(b) transition points for a given resin were similar for solvents of similar volatilities; and

(c) transition points for a given solvent decreased for resins of lower solubility.

4.3 Diffusion-Limited Period

Solvent loss in the diffusion-limited phase will be important to the medium- and long-term solvent emission properties of coatings. In the medium term, solvent diffusion in the (still) liquid coating will become more important than surface evaporation as viscosity increases with solvent loss. In the long term, solvent diffusion in a non-liquid coating film may continue for very long periods depending on molecular properties of the resin and solvent.

Hansen (1968) observed that for late-stage (low solvent concentration) drying, the diffusion coefficients of solvent molecules in polymers were exponentially related to solvent concentration (Figure 4).

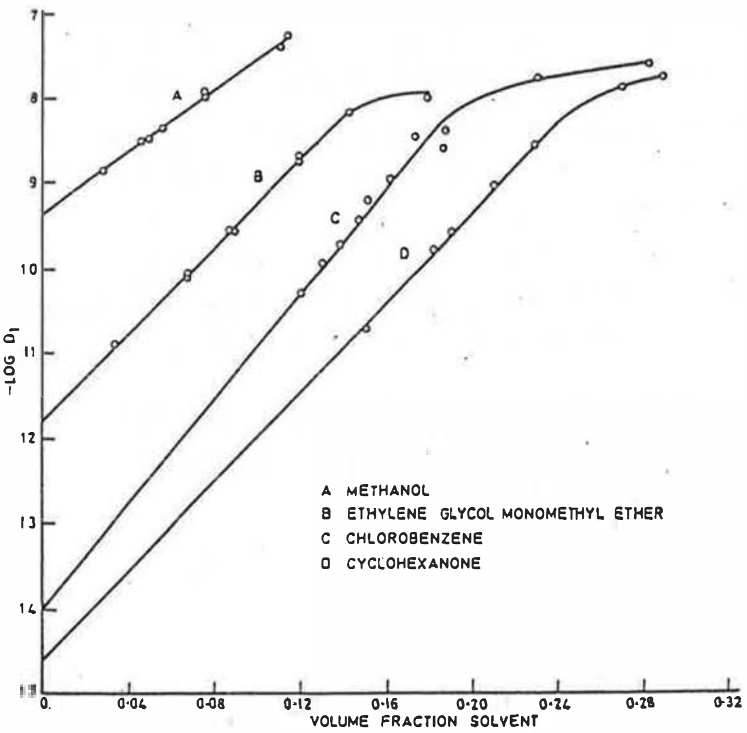

Figure 4. Diffusion coefficients in polyvinyl acetate at 25°C (Hansen 1968).

He observed that at higher solvent concentrations (and up to neat solvent) there was a separate region where D still increased logarithmically with solvent content, but much more slowly. Using mathematical models based on initial evaporation and subsequent film diffusion and employing computer evaluations, he was able to simulate the drying behaviour of solvent from PVA. He found that solvent evaporation from PVA during the film diffusion phase was described by a reduced time variable $D_o t/\ell^2$ for several solvents, where D_o is the diffusion coefficient at zero solvent concentration, t is time and ℓ is film thickness. He concluded that hydrogen and polar bonding were not important to the process, the critical factor being the solvent diffusion coefficient.

Newman and Nunn (1975) investigated solvent retention and diffusion processes in organic coatings. Reviewing early studies in this field, they noted that:

(a) some solvents were retained in polymer films at high levels (e.g. 10–20% solvent) for periods much in excess of several months;

(b) no direct relation existed between extent of retention and solvent volatility in single solvent systems;

(c) for multi-solvent systems, relative retention was markedly affected by relative volatility, lower volatility solvents being more retained (although this was likely to be due to initial volatility-limited processes that influenced solvents remaining for late-stage diffusion);

(d) hard resin films retained significant amounts of solvent over long periods (greater than several weeks) while soft resin films retained little or no solvent after short periods (approximately one week);

(e) solvent retention was reduced by inclusion of a plasticiser in the resin;

(f) rate of solvent release was increased by raising film temperature, particularly to above the Tg of the polymer.

In regard to observation (b), they found that an order for solvent retention occurred that was largely independent of the type of polymer involved. This order (Table 2) had no relationship to solvent volatility. Solvents of low molar volumes tended to be least retained but exceptions existed which were explained by molecular shape.

Table 2. An approximate order of increasing retention for individual solvents (Newman & Nunn 1975).

Solvent	Relative Evaporation Rate (n-butyl acetate = 1.0)	Molar Volume (cm^3/mole)
Methanol	4.1	40
Acetone	10.2	73
2-Methoxyethanol	0.51	79
MEK	4.5	90
Ethyl acetate	4.8	97
2-Ethoxyethanol	0.35	97
n-Heptane	3.3	146
2-Butoxyethanol	0.076	130
n-Butyl acetate	1.0	132
Benzene	5.4	88
2-Methoxyethyl acetate	0.35	117
2-Ethoxyethyl acetate	0.23	135
Dioxan	–	85
Toluene	2.3	106
Chlorobenzene	–	101
2-Nitropropane	1.5	90
m-Xylene	0.75	122
MIBK	1.4	124
Isobutyl acetate	1.7	133
2,4-Dimethyl pentane	5.6	148
Cyclohexane	5.9	108
Diacetone alcohol	0.095	123
Pent-Oxone	0.26	143
Methyl cyclohexane	3.5	126
Cyclohexanone	0.25	103
Methyl cyclohexanone	0.18	122
Cyclohexyl chloride	–	118

For example, nonplanar cyclic compounds were more retained than planar cyclic compounds (cyclohexane is more retained than benzene), and branched compounds were more retained than straight-chain compounds (isobutylacetate cf n-butylacetate). Newman and Nunn considered these effects were explained by a rate-determining mechanism of diffusion of solvent molecules through the polymer film.

Diffusion is defined as the process whereby molecules are transported from one part of a material to another by means of random molecular motion. In polymers, diffusion will depend on the molecule's size. Large molecules may require a cooperative motion of several polymer segments for diffusion to occur. Small molecules with little affinity for the polymer (eg hydrogen, oxygen in ordinary polymers and water in hydrophobic polymers) will require only very local vibrations of one or two monomer units to give a cross-section for the diffusing molecules to pass (Kishimoto 1972). They exhibit high diffusion coefficients which are generally independent of gas pressure or concentration in the polymer.

It has been found that the diffusion of solvent molecules in polymeric materials can occur by Fick's laws:

Fick's First Law

$$F = -D\frac{dC}{dx} \tag{20}$$

where F is known as the flux and is the mass of solvent per unit time passing through a plane of unit area perpendicular to the concentration gradient dC/dx, and D is the diffusion coefficient (cm^2/sec).

Fick's Second Law

$$\frac{\partial C}{\partial t} = \frac{\partial}{\partial x}\left[D\frac{\partial C}{\partial x}\right] \tag{21}$$

where $\delta C/\delta t$ is the rate of change of concentration with time.

As found by Hansen (1968), D can depend exponentially on the solvent concentration (C) by the following relationship, although other factors can complicate this dependency (see later):

$$D = D_o \exp(KC) \tag{22}$$

where D_o is the diffusion coefficient at zero solvent concentration and K is a constant.

The rate of diffusion of an organic vapour molecule in a polymer is primarily controlled by the segmental mobility of the polymer chain, a factor controlled by how far the temperature of the polymer exceeds its glass transition temperature Tg. At temperatures much above Tg microbrownian motion of polymer chains occur and they instantaneously take up an equilibrium conformation consistent with the sorbed state when a vapour molecule diffuses into the polymer. For such systems the diffusion coefficient for the polymer-vapour system is time independent and depends only on the molecule's concentration in the polymer and temperature (Kishimoto 1972).

The concentration dependence of D is complex for each polymer–solvent system with the major influencing factor being the temperature (relative to Tg). Kishimoto (1972) described the behaviour seen for many systems (e.g. polymethylmethacrylate (PMMA), polymethylacrylate,

polymethylacrylate, polyethylacrylate): at T well above Tg, log D increases linearly with concentration, the slope being smaller as T increases; as T decreases the plot becomes curved downwards at low concentrations this becoming so marked around Tg that the plot cannot be extrapolated to zero concentration without uncertainty (Figure 5).

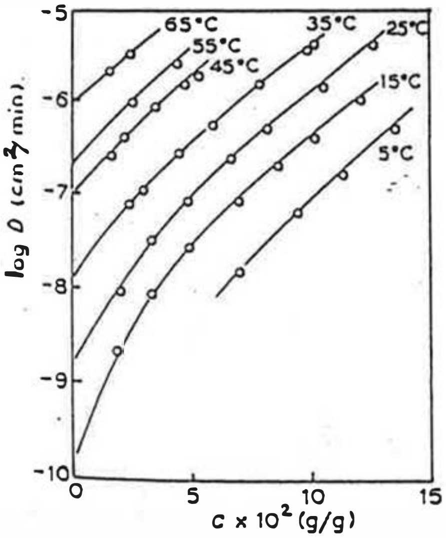

Figure 5. Concentration dependence of D for methyl acetate in polymethyl acrylate at temperatures from 5°C to 65°C (Kishimoto 1972).

Kishimoto observed that D for water vapour in polymers with low affinity for water (eg. polyvinyl acetate, polymethy acrylate, PVC) was largely independent of concentration (see Section 5.3).

If the temperature dependence of the diffusion coefficient is considered using its value at zero concentration D_o, an assumed dependence of the Arrhenius type

$$D_o = A \exp(-\Delta H_d/RT) \tag{23}$$

where R = gas constant
ΔH_d = apparent activation energy for diffusion
A = constant,

is not always found since ΔH_d may be temperature dependent, reaching a maximum around Tg (Kishimoto 1972). The effect was believed to result from an interaction between the size of the penetrant molecule and the rate of change of free volume in the polymer around Tg. It was proposed that the concentration and temperature dependence of D could be explained in terms of free volume of the system since it affects mobility of both the polymer segment and the penetrant molecule:

$$D_T = A \exp(-B_d/f) \tag{24}$$

where D_T = the thermodynamic diffusion coefficient
f = fractional free volume in the system

B_d = factor depending on the critical local free volume needed for diffusion
A = constant.

Thus, by this theory, the observed effects result from f increasing linearly with c and T. The free-volume concepts for this model (originally proposed by Fujita) and other models have been discussed by Vrentas et al (1985). They discussed in detail the Vrentas and Duda model for which they showed qualitative agreement with experiment. This model involved fluctuations in local hole free volume in response to movements of surrounding molecules. Solvent molecule motion occurred at a critical volume which was identical to the actual size of the molecule. Their expression for D_1, the solvent self-diffusion coefficient in the polymer-solvent mixture was:

$$D_1 = D_o \exp(-E/RT) \exp[-\gamma(w_1 \hat{V}_1^* + w_2 \varepsilon \hat{V}_2^*)/\hat{V}_{FH}] \qquad (25)$$

where

$$\hat{V}_{FH}/\gamma = (K_{11}/\gamma) w_1 (K_{21} + T - Tg_1) + (K_{12}/\gamma) w_2 (K_{22} + T - Tg_2) \qquad (26)$$

and $\hat{V}_{FH}$ = average hole free volume per gram of mixture
D_o = a constant
E = molar energy needed by solvent molecule to overcome attractive forces to its neighbours
γ = overlap factor accounting for the same free volume being available to more than one molecule
w = mass fraction
1,2 refer to solvent and polymer, respectively
$\hat{V}^*$ = specific critical hole free volume of component required for movement
Tg = glass transition temperature
K_{11}, K_{21} = free volume parameters for the solvent
K_{12}, K_{22} = free volume parameters for the polymer
ε = ratio of critical molar volume of solvent jumping unit to that of polymer jumping unit.

Vrentas et al (1985a) found that this model was unsatisfactory in predicting temperature and concentration variations in D, although it provided good correlation with D.

Joshi and Astarita (1979) noted that many deviations from Fick's laws occur, particularly below Tg of the polymer. They identified two non-Fickian processes:

(a) sorption of solvents into glassy polymers in which the weight of solvent sorbed varied with time to a power of 0.5 to 1.0, the extreme case (1.0) being called Case II diffusion; and

(b) desorption of solvents from swollen polymers which occurred at higher rates than sorption over the same concentration interval (whereas diffusion theory predicted smaller or equivalent desorption rate).

Typical desorption rate behaviour for solvents from swollen polymers occurred as in Figure 6.

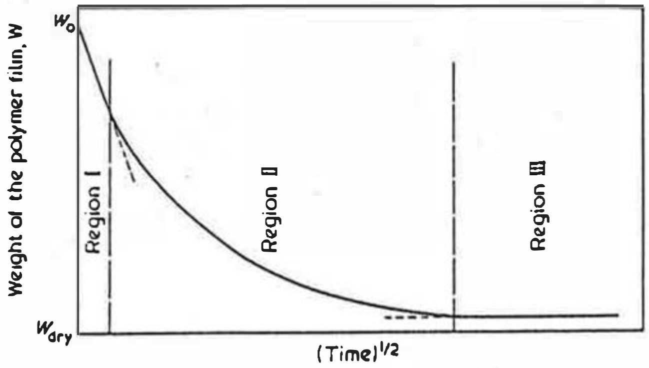

Figure 6. Weight of the polymer film *vs.* (time)$^{1/2}$ (Joshi and Astarita 1979).

Initial rate was high and proportional to (time)$^{0.5}$, but then rapidly decreased until an extremely long tail was reached. The latter showed the typical finding that not all of a solvent that went into a polymer during sorption could be desorbed. A small amount always remained in the polymer, desorbing at minute rates, and typically at a level just higher than the threshold concentration of solvent (C*) required to cause polymer swelling.

Joshi and Astarita (1979) mathematically modelled the desorption process by considering a phenomenon in which an extremely thin glassy layer of polymer (with very small diffusivity) was formed on the polymer surface. The rate process was advancement of the glassy front driven by the difference between solvent concentration at the swollen polymer front and C*. Their model assumed constant diffusivities in the glassy (D′) and swollen (D) regions and led to the following equation for rate of desorption from a semi-infinite slab:

$$\frac{dW}{dt} = -(C_o - C^*)\left(\frac{D}{4t}\right)^{1/2} \tag{27}$$

where W is the weight of the polymer film and C_o is solvent concentration at time t = 0. This predicts the Region I behaviour of Figure 6. For a finite thickness sample they assumed the asymptotic residual concentration was equal to C* and derived the following equation which predicted Region II desorption:

$$\frac{C - C^*}{C_o - C^*} = 2\sum_{0}^{\infty}\frac{(-1)^n}{(n+1/2)^{\pi}}\exp\left[\frac{-(n+1/2)\pi^2 Dt}{\ell^2}\right]\cos\left[(n+1/2)\frac{\pi x}{\ell}\right] \tag{28}$$

where n = power exponent for the solvent concentration difference that drives the rate of advance of the glassification front
ℓ = sample thickness

They noted that this equation correlated well with desorption rate data and that it predicted that if a polymer had desorbed to C* and was re-exposed to a high external activity of solvent, then it would absorb at a much faster rate than in the first cycle. It also predicted that reabsorption would proceed as a classical Fickian process. These predictions were confirmed by experimental data showing reabsorption rates up to four times faster than first absorption rates.

Case II diffusion is a solvent sorption process and as such is of limited concern to this review on solvent evaporation from polymeric coatings. Its mechanism can be considered of interest where desorption may involve similar processes. Case II diffusion has the characteristics:

(a) a sharp advancing boundary separates an inner glassy core from an outer swollen and rubbery shell;

(b) the swollen gel behind the advancing penetrant front is almost in equilibrium;

(c) the gel-glassy core boundary advances at a constant velocity; and

(d) an induction time exists before Case II diffusion commences.

Lasky et al (1988) described the Thomas and Windle model which assumed that as the penetrant diffused into the polymer it created a thermodynamic (osmotic) pressure, which in turn created "sites" for more penetrant. They found good experimental fit to this model when it was modified to allow polymer viscosity to decrease exponentially with osmotic pressure, and to include an initial volume fraction of rapidly filling interstitial sites, taken to be the initial free volume.

Dodin (1981) evaluated the kinetics of non-Fickian solvent desorption from polyvinyl alcohol solutions (usually in water or water plus methanol). A thermoactivation theory of diffusion was used as the basis for the study, according to which the following correlations applied:

$$t \sim 1/D \sim \exp(Q/RT) \tag{29}$$

where t = time to obtain a definite quantity of residual solvent
Q = effective activation energy of diffusion which depends on the quantity of residual solvent C
T = temperature
D = diffusion coefficient

Dodin proposed a mechanism in which desorption during late-stage drying at different temperatures would be linear with log time and would converge at a specific concentration (Figure 7). This behaviour had been observed for amorphous polymers such as polycarbonate and polysulfone, the late-stage diffusion of which were described by:

$$t = \beta \exp\left[\frac{Q_o - \alpha C}{R}\left(\frac{1}{T} - \frac{1}{T_P}\right)\right] \tag{30}$$

where α, β = constants
C = concentration of solvent in film
Q_o = activation energy of diffusion at $C = 0$
T_P = temperature at which straight lines intersect in log t vs 1/T

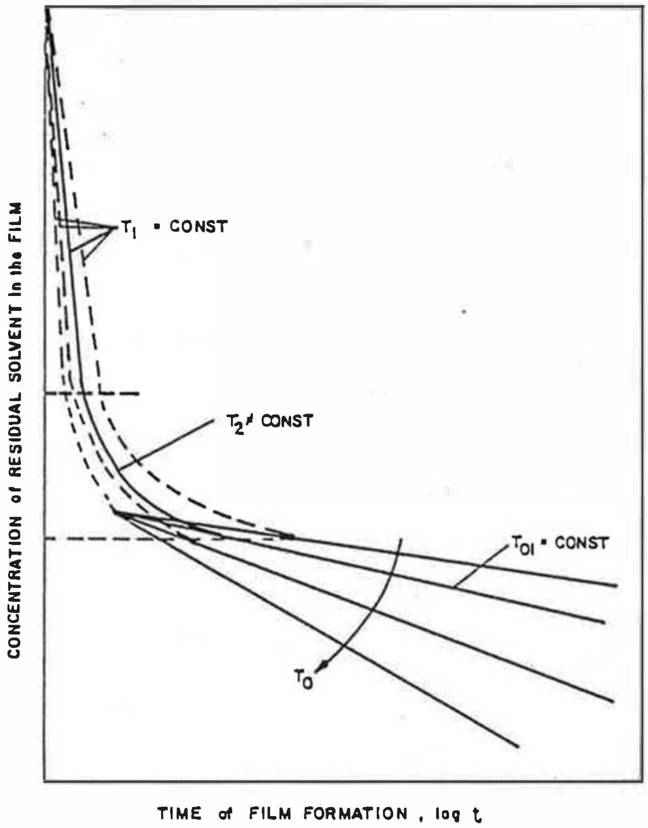

Figure 7. Desorption curves at different temperatures of film formation. T_{01} is temperature in the drying chamber; T_1 is temperature on the surface of the film during the first stage; T_2 is temperature of the film during the period of change of the mechanism of solvent transport (Dodin 1981).

Dodin found that desorption of water and methanol from polyvinylalcohol occurred by slightly different relationships, probably due to the partly crystalline nature of the polymer:

$$t = \beta \exp\left[\frac{Q_o - \alpha \log C}{R}\left(\frac{1}{T} - \frac{1}{T_P}\right)\right] \tag{31}$$

$$Q(C) = 2.3R\frac{\Delta \log t}{\Delta(10^3 / T)} \tag{32}$$

A similar mechanism of diffusion was proposed for all cases – thermal fluctuations which created the conditions for molecules to overcome a potential barrier Q. However the values found for Q_o of polyvinylalcohol were greater than found for other systems and this was considered to result from physical (hydrogen) bonding between polymer and solvent. Both α and Q_o were defined by the polymer-solvent system and were correlated by the following equation derived from equation (31) at the intersection point (where $C = C_{lim}$):

$$Q = Q_o - \alpha \log C_{lim} = 0 \tag{33}$$

C_{lim} was observed to be constant (≈20% w/w) for polycarbonate, polysulfone and all polyvinyl alcohol-based systems, leading to direct proportional changes in values of Q_o and α.

Blum and Pickup (1987) investigated self-diffusion coefficients for several solvents in polystyrene solutions from 0 to 80% polymer using a pulsed-gradient spin-echo NMR method. A plot of the normalized solvent self-diffusion coefficients

$$\left(\frac{D(1-V_p)}{D_{solvent}}\right)$$

relative to the volume fraction of polystyrene (V_p) provided a universal curve for all solvents and temperatures (Figure 8).

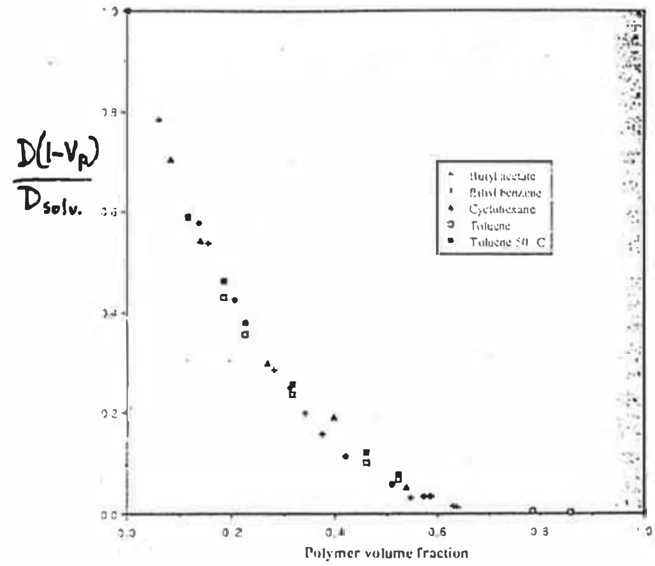

Figure 8. Normalized solvent self-diffusion coefficients for several solvents as a function of the volume fraction of polystyrene for the lower concentration region. The measurements were made at 25°C except for one toluene-containing sample which was at 50°C (Blum & Pickup 1987).

This showed that specific chemical interactions played no role in solvent diffusion in this region and that diffusion coefficients could be predicted from the diffusion coefficient of the pure solvent at a given temperature and the volume fraction of polymer.

They found that diffusion coefficients at polymer contents of 80 to 95% w/w were very much smaller and exhibited Arrhenius-like temperature dependence (ie. plots of -log D versus 1/T were linear for each polymer content and exhibited similar activation energies at each content).

4.4 Overview and Integrated Models

It is clear that the drying of solvent-based coatings is a complex and multi-mechanistic process dominated initially by solvent volatility and later by solvent diffusion in semi-dry films. Volatility is important up to resin contents where solvent diffusion in the increasingly viscous liquid film becomes limiting, for example, at 40–50% by volume resin for alkyd coatings. Initial high rates of solvent evaporation, similar to those found with neat solvents, have been observed in this region. The major factors influencing initial solvent evaporation rate (W′) are shown in the equation:

$$W' = k_v T^{1/2} p_o \tag{4}$$

where k_v = mass transfer coefficient at any velocity v
T = absolute temperature
p_o = vapour pressure of the solvent at T

k_v will depend on solvent molecular weight and surface air velocity (v), the latter dependence being linear or the more complex:

$$k_v = k_o + \frac{v}{Av + B} \tag{5}$$

Evaporation of solvent mixtures will be complicated since, by Raoult's law, the vapour composition will differ from the liquid composition, causing the latter to change continuously during drying. Changing liquid composition will cause solvent interactions (where they exist) to change, varying the empirical "escaping coefficients" of solvents and further complicating the prediction of evaporation rates.

Proportionalities for wet phase drying of paints under volatility-limited conditions are of the form:

$$W' \propto D_v, D_f, \ell^{-1}, T^{-0.5} \text{ (or } e^{-1/T}\text{)}, (c_i - c)$$

where D_v = vapour diffusivity of solvent
D_f = solvent diffusivity in the paint film (usually $D_f >> D_v$ under volatility-limited drying)
ℓ = paint film thickness
c_i = solvent concentration at the air-coating interface
c = solvent concentration in the bulk of the gas
T = temperature

Proportionalities for the transition period are less clear since volatililty- and film diffusion-limited processes occur in similar (but continually varying) proportions. One relationship of the following form has been demonstrated

$$\log\left(\frac{1-C}{C}\right) = \alpha t \tag{19}$$

where C = solvent concentration in the film at time t
α = empirical constant for the specific coating

The film diffusion limited phase will occur at a rate primarily dependent on the temperature of the film, especially in relation to the glass transition temperatures (Tg) of the polymer and polymer/solvent system. Specific chemical interactions may also play a role for some polymer-solvent systems. The diffusion process by Fick's first law meets the relationship

$$F = -D\frac{dC}{dx} \tag{20}$$

where the flux F is the mass of solvent per unit time passing through a plane of unit area perpendicular to the concentration gradient dc/dx. However D may vary continuously throughout the drying process by a logarithmic relationship with C

$$D = D_o \exp(KC) \qquad (22)$$

provided the film temperature exceeds Tg; around Tg, D decreases sharply at low C and no longer meets this relationship. D_o can exhibit an Arrhenius-type temperature dependence:

$$D_o = A \exp(-\Delta H_d/RT) \qquad (23)$$

but not always since the apparent activation energy ΔH_d can be temperature dependent, reaching a maximum around Tg. The fundamental relationship for values of D is

$$D = \text{constant} \exp(-B_d/f) \qquad (24)$$

where f = fractional free volume in the system
B_d = factor dependent on the critical local free volume needed for diffusion

Thus, the observed effects on D result from f increasing linearly with c and T.

Some of the practical implications found for diffusion-limited evaporation are:

(a) solvent evaporation for one coating at different thicknesses and with different solvents will be reduced to one curve when assessed by the reduced variable D_ot/L^2;

(b) solvent evaporation will be slower from resins of higher Tg;

(c) solvent evaporation will be significantly enhanced if the coating is heated above Tg of the resin;

(d) solvent evaporation will be slowest for solvents of high molar volume and non-planar shape;

(e) there will be no influence of solvent volatility.

Blandin et al (1987, 1987a) considered paint drying to involve two processes, viz. diffusion of the solvent through the polymer and solid ingredients and evaporation of solvent from paint surfaces. Diffusion of solvent in the paint film was assumed to occur according to Fick's law governed by a diffusivity D which varied with temperature and solvent concentration. For a specific high-solids paint formulation (22–35% solvents), they empirically determined these effects using the relationships:

$$\frac{M_t}{M_\infty} = \frac{2}{\ell}\left[\frac{Dt}{\pi}\right]^{0.5} \qquad (34)$$

where M_∞ and M_t = loss in weight at infinite time and time t, respectively
ℓ = paint film thickness

and

$$D = D_o \exp\left(-\frac{\alpha}{C}\right) = \beta \exp\left(-\frac{\gamma}{T}\right) \exp\left(-\frac{\alpha}{C}\right) \tag{35}$$

where D_o = diffusivity at $C = 0$
C = concentration of solvent in paint film
α, β, γ = empirical constants

The rate of solvent evaporation was found to vary with temperature in proportion to the vapour pressure of solvent, yielding an empirical relation:

$$W' = X \exp\left(-\frac{Y}{RT}\right) \tag{36}$$

where T is temperature (°K) and X and Y are empirical constants.

By use of these relationships in a model based on a numerical method with finite differences, they were able to predict the drying behaviour of the high-solids paint up to 48 hours under a range of conditions. While this demonstrated the importance of solvent diffusion in the paint film and solvent evaporation from the paint surface, the model was limited to interpolating the drying behaviour of specific paint for which empirical data had been predetermined.

Rosen and Anderson (1990) experimentally determined the drying rates of paints (generally containing approximately 50% alkyd resin by weight) in a laminar flow chamber at controlled temperature, humidity and surface air velocity (generally 0.03 to 0.2 m/sec). Solvent emission flux W' (mass/area.time) in the first 60 minutes was the main factor evaluated. In most cases W' decreased over this period and Rosen and Anderson concluded that diffusion of solvents in the paint layer governed solvent transport for the whole drying process. This contradiction to other studies which have found solvent volatility to predominate initial drying behaviour may be due to the high resin content of the paints that were evaluated.

Waggoner and Blum (1989) developed a computer model for paint drying which used both solvent volatility and film diffusion factors. They used two fundamental equations. Volatile evaporative flux was determined by multiplying the standard rate of evaporation of the pure solvent $\left(R_e^o\right)$ by its activity:

$$W' = R_e^o (a - p') \tag{37}$$

where a = activity of the solvent in the surface layer of the film, and
p' = relative vapour pressure of solvent = partial pressure of solvent in the air divided by its partial pressure at saturation (= zero under most conditions).

Values of R_e^o were taken from literature, were determined experimentally under the same conditions as paint drying or were calculated from:

$$R_e^o = p_v (M/2\pi RT)^{0.5} \exp(-s/y) \tag{38}$$

where p_v = vapour pressure of solvent,
s = height solvent molecule must rise above the film before air currents sweep it away ($s = 0.25$ cm for coating on a flat plate),
y = mean free path of the solvent molecules.

Values of a were determined from the Flory-Huggin's equation

$$\log_e a = \log_e \phi + (1 - 1/m')(1 - \phi) + X(1 - \phi)^2 \tag{39}$$

where ϕ = solvent volume fraction in the surface layer of the film,
X = Flory-Huggin's interaction parameter
m' = ratio of molar volumes of polymer to solvent (generally $1-1/m' \approx 1$)

Diffusion of the solvent in the paint film was estimated using Fick's second law:

$$\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2} \tag{21}$$

but with the film divided into several layers, each assumed to be uniform for a given time step and the concentration expanded as a function of time:

$$\left(\frac{\partial C}{\partial t}\right)_{i,j} = \left(C_{i,j+1} - C_{i,j}\right) / \Delta t \tag{40}$$

where i refers to a given layer and j refers to the layer at the beginning of a time step and (j + 1) the same layer at the end of the time step. Concentration was also expanded as a function of position, yielding:

$$\left(\frac{\partial^2 C}{\partial x^2}\right)_{i,j} = \frac{1}{2}\left[\left(C_{i+1,j} - 2C_{i,j} + C_{i-1,j}\right)/(\Delta x)^2 + \left(C_{i+1,j+1} - 2C_{i,j+1} + C_{i-1,j+1}\right)/(\Delta x)^2\right] \tag{41}$$

Substitution of these equations into Fick's second law yielded:

$$-r\, C_{i-1,j+1} + (2 + 2r)\, C_{i,j+1} - r\, C_{i+1,j+1} = r\, C_{i-1,j} + (2 - 2r)\, C_{i,j} + r\, C_{i+1,j} \tag{42}$$

where $r = D_i\, t/h_i^2$ and t is the time interval, h_i the thickness of the layer and D_i the diffusion coefficient of solvent in the i^{th} layer.

For each time step, the mass of solvent that escaped the top layer was determined and the amount of solvent in the top layer reduced by this amount. Diffusion of solvent within each successive layer was determined for the time step and then the process repeated for further time steps.

Diffusion coefficients were experimentally determined for polystyrene with 15 to 100% by volume toluene at different temperatures. Extrapolation to the higher solids region required use of the Vrentas–Duda solvent diffusion equations, described earlier. A comparison of experimental and predicted (based on five layers) drying of a 90 µm film of polystyrene in 88% by weight toluene is shown in Figure 9. Good agreement is seen for the 100 minute time span considered. It is unknown whether this would extend to longer drying times.

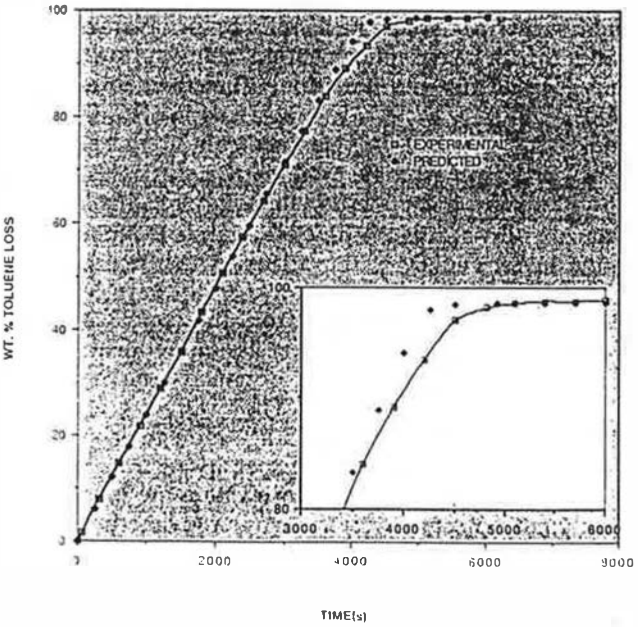

Figure 9. Comparison of experimental and predicted drying of 90 µm film of polystyrene in 88% toluene (inset shows transition region Waggoner & Blum 1989).

5. DRYING MECHANISMS FOR WATER–BASED LATEX PAINTS

Drying mechanisms for water–based latex paints can be expected to differ somewhat from those of solvent–based resin solution coatings since:

(a) with water as the major volatile constituent, ambient relative humidity will significantly influence water evaporation relative to that of cosolvents (see Section 3.3.2.2);

(b) as a two-phase material with the volatiles distributed differently in each phase, latex paint drying will be complicated by distribution coefficients and the physical processes during conversion to a single film phase;

(c) latex paints will contain coalescing solvents with much lower diffusivities than the solvents used in solvent–based paints.

5.1 Volatility–Limited Period

Vanderhoff et al (1973) observed that water evaporated from latex coatings initially at a constant rate similar to that of water alone. However water evaporation slowed markedly when the polymer volume fraction increased to 60–75%, the point at which the latex particles came into contact and the water–air interfacial area decreased.

Hansen (1974) measured the rate of loss of water and VOCs (cosolvents and coalescing solvents) from water–based polyvinyl acetate latex coatings of different thicknesses and drying periods up to 200 hours. He reasoned that if drying involved film diffusion processes, then volatile (i.e. water and solvents) loss rates should be reduced to a common curve when plotted against t/ℓ^2, where t is time and ℓ is film thickness. If surface evaporation controlled the drying process, then volatile loss rate vs t/ℓ would be a common curve. Hansen observed the latter to be the case for water loss, glycol loss and coalescing solvent loss, each of these occurring independently and sequentially during the drying process (Figure 10).

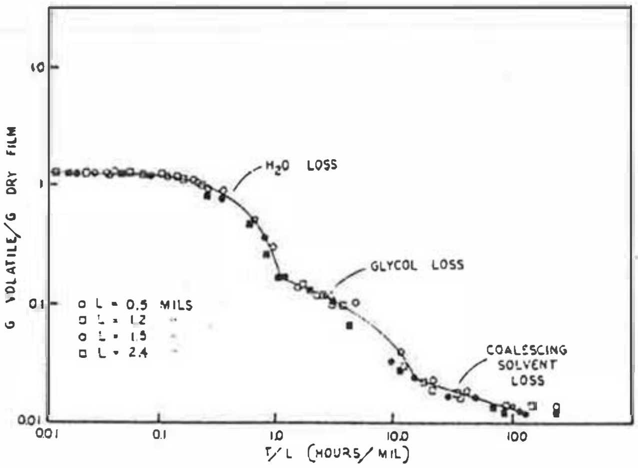

Figure 10. Loss of volatile from latex paint films (Hansen 1974).

This long–term behaviour of the coalescing solvent contrasted with the long–term loss of solvent from resin solution coatings, where a reduced time variable of t/L^2 was found, indicating a diffusion-controlled process. Hansen concluded that for latex paints, the rates of <u>all</u> volatile losses were controlled by surface evaporation processes and that individual compound evaporation rate data would give a good relative indication of paint drying rates. As described in Section 3.4.2, the development of cohesive films from latexes (at which stage film diffusion processes might be expected to dominate) can take several tens of hours. Hansen's findings suggest a cohesive film was not formed within the 200 hour period of investigation.

Dillon (1977) described the theoretical basis for water–solvent azeotropy and critical relative humidity, as described in Section 3.3.2. The rate of loss of component i, dWi/dt, was assumed to follow first order kinetics with modification for relative vapour saturation:

$$\frac{dWi}{dt} = -A\, R_i^{v,T}(\gamma_i x_i - \rho_i) \qquad (37)$$

where A = vapour liquid interfacial area

$R_i^{v,T}$ = rate of evaporation of pure i at air velocity v and temperature T

γ_i = activity coefficient of i

x_i = mole fraction of i

ρ_i = relative vapour saturation of i (= relative humidity for water)

The temperature dependence of $R_i^{v,T}$ was calculated by the Gardner equation:

$$R_i^{v,T} = k_{i,v}\, T^{1/2}\, P_{i,T} \qquad (4)$$

where $P_{i,T}$ = vapour pressure of pure i at temperature T

$k_{i,v}$ = mass transfer coefficient at air velocity v = $k_{i,o} + \dfrac{v}{\alpha_i v + \beta_i}$ (5)

α_i, β_i = air speed coefficients for the mass transfer coefficient

α_i and β_i were calculated by first determining the empirical constants for evaporative flux at a temperature T:

$$R_i^{v,T} = R_i^{o,T} + \frac{v}{A_{i,T}v + B_{i,T}} \qquad (43)$$

and then determining α_i and β_i from:

$$\alpha_i = A_{i,T}\, T^{1/2}\, P_{i,T} \qquad (44)$$

$$\beta_i = B_{i,T}\, T^{1/2}\, P_{i,T} \qquad (45)$$

Since α_i and β_i were constants, these equations also expressed the temperature dependences of $A_{i,T}$ and $B_{i,T}$.

The temperature dependence of vapour pressure was found using the Antoine equation:

$$\log_{10} P_{i,T} = a_i - \frac{b_i}{\tau + c_i} \tag{46}$$

where τ = Celsius temperature
a_i, b_i, c_i = Antoine constants

Dillon derived that the composition of a binary evaporating mixture would not change if:

$$\frac{R_1^{v,T}}{M_1}\left(\gamma_1 - \frac{\rho_1}{x_1}\right) = \frac{R_2^{v,T}}{M_2}\left(\gamma_2 - \frac{\rho_2}{x_2}\right) \tag{47}$$

where M_1 and M_2 are the molecular weights of components 1 and 2 respectively. This equation states that the components will not vary in composition if their molar evaporation rates, modified by $(\gamma - \rho/x)$, are equal.

For the special case of water (w) plus an organic (o) cosolvent, critical relative humidity (CRH) is defined by

$$CRH^{v,T} = x_w\left(\gamma_w - \frac{R_o^{v,T}\gamma_o M_w}{R_w^{v,T} M_o}\right) \tag{48}$$

Eaton and Willesboorde (1980) applied Dillon's kinetic equations to describe the early evaporative behaviour of water and cosolvents from waterborne (water–soluble and water–dispersed) coatings. Considering $(\gamma_i x_i)$ in equation (37) as the thermodynamic activity of i, they calculated it for water in a polymer/water mixture from Flory–Huggins polymer solution theory:

$$\log_e(\gamma_w x_w) = \log_e \phi_w + \left(1 - \frac{1}{m'}\right)(1 - \phi_w) + X_{12}(1 - \phi_w)^2 \tag{39}$$

where ϕ_w = volume fraction of water
X_{12} = Flory–Huggins interaction parameter (calculated from solubility parameters or, preferably, measured experimentally)
m' = ratio of molar volumes of polymer to water.

Using these equations, they were able to predict the initial (4–6 hours) drying of water from a coating.

Stratta et al (1978) investigated the evaporation behaviour of several common cosolvents used in water–based paints. Simple water–cosolvent systems exhibited non–ideal evaporating characteristics, i.e. they departed from Raoult's Law. This non–ideality was expressed in an apparent activity coefficient γ_i (as defined in equation 12). For Raoult's Law, $\gamma_i = 1$. Stratta et al found that γ for water ranged 0.81 to 0.95, averaging 0.91 while γ for cosolvents were generally much greater than unity (i.e. they evaporated much faster than predicted from ideal solution behaviour). Further since γ would change with composition, they determined Wilson parameters for each cosolvent in water using the relationship:

$$\log_e \gamma_i = 1 - \log_e\left[\sum_{j=1}^{N} x_j A_{ij}\right] - \sum_{k+1}^{N}\left[\frac{x_k A_{ki}}{\sum_{j=1}^{N} x_j A_{kj}}\right] \qquad (49)$$

where A_{ij} = temperature–dependent Wilson parameter for the ij binary, and

x = liquid phase mole fraction.

This and earlier equations were used to computer simulate the drying behaviours of a range of coatings.

Rocklin (1986) discussed practical aspects of water/cosolvent "pseudo-azeotropes" relevant to the selection of cosolvents for optimal drying. Azeotropy occurs in a binary blend when:

$$P_1^o \gamma_1 = P_2^o \gamma_2 \qquad (50)$$

where P_1^o, P_2^o = vapour pressures of pure compounds

γ_1, γ_2 = activity coefficients for pure compounds

Rocklin noted that in most cases the azeotrope had the highest vapour pressure (and fastest evaporation rate) of all component mixtures. He was able to predict azeotropes for solvent mixtures by determining evaporation rates (R) from

$$R_{12} = R_1^o x_1 \gamma_1 + R_2^o x_2 \gamma_2 \qquad (51)\ (\text{also } (12))$$

where x_i = mole fraction of component i

R_i^o = evaporation rate of component i (eg. from Shell Automatic Thin Film Evaporometer)

Activity coefficients for equation (51) were calculated using the UNIFAC method for computing γ as the solvent concentrations changed during evaporation. For aqueous blends the driving force for water evaporation into humid air was considered to be the difference between the partial pressure of water above the blend and the partial pressure from ambient relative humidity. Using this correction Rocklin predicted and evaluated water–cosolvent pseudo azeotropes for use in water–reducible coatings. For example, 2–butoxyethanol (ethylene glycol monobutyl ether EGBE) was found to be a particularly efficient azeotroping cosolvent even though it evaporated five times more slowly than water. At all relative humidities (up to 80% RH) blends of up to 20% EGBE evaporated faster than water at the same humidity. It was found that 90% evaporation times of cosolvents provided no indication of their azeotroping effectiveness.

Kornum (1982) critically reviewed mass– and heat–transfer theories for the evaporation behaviours of solvents and water–cosolvent systems for coatings and compared them with experimental observations. General agreement was found, and although sometimes these were only qualitative, the theories were capable of indicating the impact of physical parameters on evaporative behaviour. Water evaporation varied linearly with ambient RH although, under assumed isothermal conditions, a diffusion boundary layer thickness of 35 mm was estimated in the absence of forced convection. This was considered unrealistically high and was taken to indicate that heat–transfer was also rate limiting. A surface temperature depression of 2°C was found to occur and when this was accounted for, a boundary layer thickness of a few millimetres was estimated. Under the conditions described, the relative evaporation rate (R_e) of water (relative to n-butylacetate, R_e=100) was given by

$$R_e\,(\text{water}) = 80\left(1-\frac{\text{RH}}{100}\right) \tag{52}$$

Theoretically, the evaporative mass flux was predicted to be proportional to the square root of air velocity within the region of laminar flow, considered to be likely in the drying of coatings. Kornum noted that Yoshida (1972) had measured proportionality with air velocity for several solvents and suggested this resulted from non-laminar and complex air flow characteristics of the experimental apparatus. Other studies had found proportionality to the square root of air velocity for evaporation of water and organic solvent.

The minimum air flow involved in any evaporation process will be free convection caused by buoyancy changes from density variation with temperature and composition of the gas layer above the film. Free convection will always be superimposed on forced air flow but Kornum estimated that under the practical conditions of drying of water and solvents, forced convection would be the sole significant flow only when air velocities exceeded 0.1 m/sec parallel to drying surfaces.

Kornum noted that the heats of evaporation for most organic solvents were similar so that relative evaporation behaviour was mainly independent of temperature. However water has a significantly larger (approximately five-fold) heat of evaporation and so its evaporation rate (at a given RH) will diminish relative to that of solvents as temperature increases. This explained the decreased CRH with increasing temperature observed by Dillon (1977). A further consequence was that as air velocity was increased and surface cooling occurred, water concentration at the film surface decreased more than that of organic volatiles, leading to the relatively slower evaporation of water.

Kornum observed that water evaporated initially from latex paints at the same rate as pure water and that evaporation rates exhibited proportionality to the square root of air velocity (Figure 11) except below 0.1 m/sec where free convection was seen to take over. For practical purposes, an empirical linear relation could be applied above this velocity.

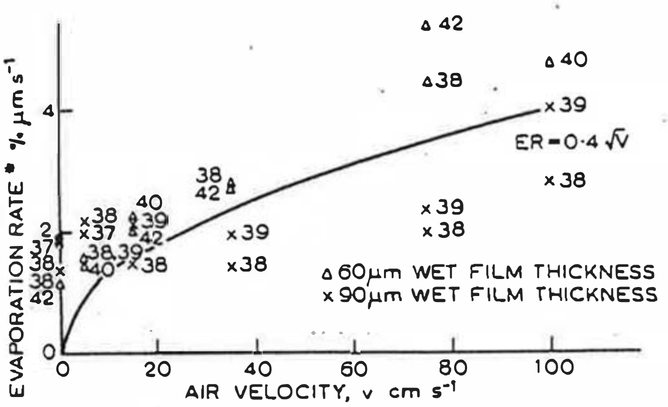

Figure 11. Evaporation rate for a white latex paint as a function of air velocity in parallel flow. The curve indicates the expected proportionality between evaporation rate and square root of air velocity when forced convection dominates the air flow. The number at the measured values indicates the relative humidity during measurement. *(remaining solvent x film thickness)/(solid content x time) (Kornum 1982).

He showed that established procedures for estimating the quantities of film constituents during evaporation were applicable to mixtures of water and organics by applying a relative evaporation rate for water which varied proportionally with relative humidity, as described earlier. For the limited cases evaluated, ideal behaviour was exhibited. However when polymer latex particles were also present, solvent partitioning to the polymer during drying led to more complex and non-ideal behaviour.

5.2 Diffusion–Limited Period

To some degree, the diffusion of organic solvents in a coalesced latex film can be expected to resemble diffusion of solvents in films from solution coatings. However the degree to which coalescence has occurred (see Section 3.4.2) and a plasticising effect of residual water are factors that may limit this comparison.

As a result of the latter factor, the rate of diffusion of water from paint films may be an important criterion for organic loss. Water diffusion in polymers has been observed to exhibit two types of behaviour (Kishimoto 1972). When the affinity of water for the polymer is very low (polyvinyl acetate, polymethyl acrylate, polyvinyl chloride and polyoxymethylene), the diffusion coefficient shows no or slight concentration dependence (Figure 12), temperature being the main controlling factor. By contrast, for hydrophilic polymers (ethyl cellulose, polymethylmethacrylate polyurethane) the water diffusion coefficients were found to decrease with concentration of water. This was considered to result from clustering of water molecules in these polymers and the greater energy needed to cause them to become mobile.

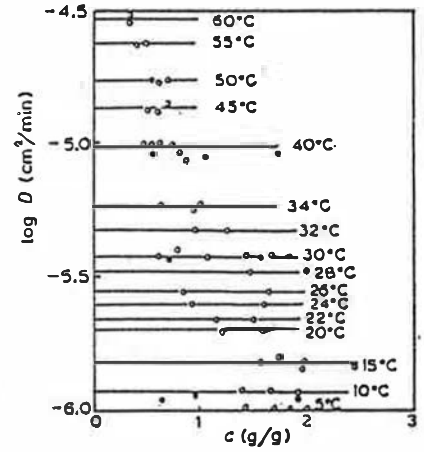

Figure 12. D for polyvinyl acetate-water at different temperatures (Kishimoto 1972).

Okazaki et al. (1974) determined the water diffusion coefficients for a polyvinyl alcohol aqueous solution over a wide concentration range (Figure 13). This resembled the typical diffusion behaviours seen for organic solvents (see Section 4.3).

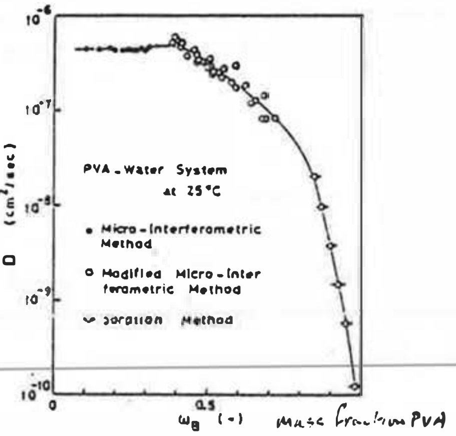

Figure 13. Diffusion coefficients of polyvinyl alcohol aqueous solution (Okazaki et al. 1974).

Overall it is expected that water diffusion from low-affinity polymers will be rapid and independent of concentration, while from hydrophilic polymers it will be markedly slower and strongly concentration-dependent.

Eaton and Willeboordse (1980) discussed free volume theory for calculating the diffusion coefficients (D) of water in a polymer where coefficients varied with water content. Water was considered to act as a plasticiser for the polymer by contributing an amount of "free volume" to the system:

$$D = D^{o} \exp\left[-V^{*}\left(\frac{1}{f} - \frac{1}{f_{w}}\right)\right] \qquad (53)$$

where D° = self-diffusion coefficient of water in water
V^{*} = factor related to the size of the diffusing (water) molecule
f = total free volume of solvent-polymer system
f_w = free volume of pure water

f was determined from:

$$f = \phi_p f_p + \phi_w f_w \tag{54}$$

where f_p = free volume of pure polymer,

ϕ_p, ϕ_w = polymer and water volume fractions.

Combining these equations

$$\log_e\left(\frac{D}{D^{\circ}}\right) = \beta\gamma(1-\alpha)/(1+\alpha\gamma) \tag{55}$$

where γ = $(1-\phi_w)/\phi_w$

α = f_p/f_w

β = V^{*}/f_W

They reported that α and β were found to be 0.5 and 4.5, respectively, for water in polymers (type unspecified).

Dodin (1981) evaluated the late-stage drying of polyvinyl alcohol solutions in water/methanol mixtures (as described in Section 4.3) at different temperatures and found they were linear on a log/log basis and converged at a specific time (Figure 14). This was considered to result from the greater importance of ambient temperature to late-stage drying when free liquid evaporation (and related film cooling) had been completed.

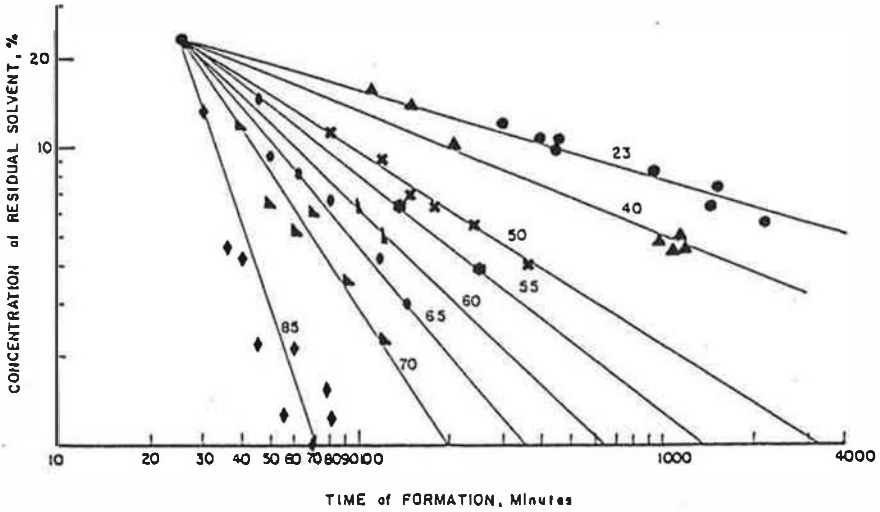

Figure 14. Residual solvent concentration as a function of the time of film formation for polyvinyl alcohol + water + methanol system. Numerals near straight lines are temperatures of formation in °C (Dodin 1981).

The equation describing this behaviour was shown to be:

$$t = \beta \exp\left[\frac{Q_o - \alpha \log C}{R}\left(\frac{1}{T} - \frac{1}{T_p}\right)\right] \qquad (56)$$

where α, β = empirical constants,
Q_o = activation energy of diffusion when solvent concentration in the film, C, was zero,
Tp = temperature at which straight lines intersected on a log t vs 1/T plot

Dodin noted that this equation was applicable only at solvent concentrations below 20% by weight (Figure 14) since at higher concentrations solvent transfer to the evaporation surface probably occurred by self-diffusion.

These studies have generally considered water and cosolvent diffusion through a continuous polymer film which was originally soluble in the water-solvent mixture. Water and cosolvent diffusion in late-stage drying of latex films will be complicated by residual (discontinuous) latex structure and formulation components, but has received less investigation. Vanderhoff et al (1973) measured the water permeabilities of several cast films from latex coatings within hours of preparation (when deformed latex spheres were clearly visible by electron microscopy) and after aging for periods much in excess of 14 days (the period in which coalescence of latex particles was generally completed). The latter were comparable to values reported for continuous polymer films while the former were significantly (up to 1000 times) greater. It was concluded that water loss from the just "dry" film occurred by diffusion through capillary channels within the film rather than through the polymer itself. However as coalescence proceeded (over a period of several days) the water loss rate slowed and diffusion through the polymer became the dominant mechanism.

6. STUDIES OF VOC EMISSIONS FROM COATINGS

VOC emissions from paints have been studied in chamber experiments (usually small scale) to estimate emissions to indoor air or in building experiments to determine occupational exposures at paint application.

6.1 Small-Scale Emission Studies and Models

6.1.1 Current guidelines

Various emission experiments and models carried out over the last 10 years have resulted in the development of general guidelines for "small-scale environmental chamber determinations of organic emissions from indoor materials/products" (ASTM 1996, CEC 1991). Small scale chambers are less than 5 m^3 in volume (usually less than 1 m^3) and can only be used to assess:

(a) small samples taken from larger materials rather than complete items, and

(b) post-application emissions from wet materials.

However within these limits they provide data for the screening, ranking and selection of products, for guiding field studies and determining effects of environmental variables on emission, and for use in models to predict indoor air pollutant concentrations. Specific features of environmental chambers are essential to their use and are specified in guidelines, e.g.:

(a) constructed from materials that are non-adsorbent, non-emitting, chemically inert and smooth, so as to not interfere with material emission processes;

(b) well-mixed interior space;

(c) supplied with purified air such that concentrations of individual VOCs are less than 2 $\mu g/m^3$ and total VOC (TVOC) concentration less than 10 $\mu g/m^3$;

(d) tight quality control on environmental conditions and concentration measurements such as:

Parameter	Precision	Accuracy
temperature	±0.5°C	±0.5°C
relative humidity	±5.0%	±10%
air flow rate	±1.0%	±2.0%
sample area	±1.0%	–
sample (wet) weight	±10.0%	–
VOC concentration	±20% RSD	–
emission rate	±20% RSD	–

(e) product loading rates selected to be representative of field use of the products e.g. for sheet products: area of product/chamber volume, and

(f) for volatility-limited emissions, testing should be carried out under typical indoor air velocities (0.05 to 0.1 m/sec). It will be noted (later) that many chamber experiments have been carried out without forced air velocities. However, as discussed in Section 5.1, Kornum (1982) theoretically predicted that evaporation from typical surfaces below air velocities of 0.1 m/sec was controlled by free convection caused by buoyancy effects. He also observed this effect for drying of water-based latex paints (Figure 11), the evaporation rate under free convection being similar to that at 0.1 m/sec. It is possible, then, that chamber experiments carried out without forced air velocities have been representative for velocity conditions found in buildings.

Chamber emission studies are carried out by placing the source product within the chamber and measuring the pollutant concentrations in the chamber air for a period of days to weeks to provide time-concentration data. It has been found that such specific data is needed since many common indoor materials exhibit large decreases in emission flux over time. This data can be handled in several ways depending on the characteristics of the source emission. For any experiment, source emission can be described by an emission rate from the chamber (ER, mass/time) and an intensive property of the source, its emission flux (EF, mass/area/time) where

$$ER = A\,(EF) \qquad (57)$$

and A is source area.

A source that has a constant emission flux will exhibit the following pollutant concentration (c) in the chamber:

$$c = L(EF)\,[1 - \exp(-Nt)]/N \qquad (58)$$

where L = loading rate (source area/chamber volume)
N = air change rate of chamber.

At large times this simplifies to:

$$c = L\,(EF)/N \qquad (59)$$

i.e. an equilibrium concentration is reached in the chamber from which EF is easily determined.

A source with a variable emission factor over time can be evaluated to determine empirical emission fluxes at specific times:

$$EF_t = (\Delta c_t/\Delta t + Nc_t)/L \qquad (60)$$

where c_t = pollutant concentration at time t

Or may be evaluated to determine if its emission pattern fits a specific mathematical expression (source model). A source model commonly found for drying materials has been first order decay:

$$EF = (EF_o)\,\exp(-kt) \qquad (61)$$

where EF_o = emission flux at time t = o, and
k = first order rate constant

and for this model chamber concentration will vary as:

$$c = L(EF_o)\,[\exp(-kt) - \exp(-Nt)]/(N-k) \qquad (62)$$

However the chamber interior can act as a sink for some VOCs, adsorbing and desorbing them throughout the experiment, thereby influencing c. More sophisticated models to deal with this process have been developed and will be discussed before chamber emission experiments are reviewed.

The foregoing discussion has related to small environmental chambers into which the samples are placed. An alternative approach is a micro-chamber called the Field and Laboratory Emission Cell (FLEC) (Wolkoff *et al.* 1991) designed after a review of small environmental chambers (Gustafsson and Jonsson 1991). This is a portable stainless steel cone-shaped cell. The cell has an open face which is placed against flat surfaces (area 177 cm^2) from which emissions are measured (generally after an operation period of 24 hours). The cell volume is 35 mL and the typical ventilation rate (N = 1870 h^{-1}) and loading factor (L = 506 m^2/m^3) are significantly greater than encountered under field conditions, while surface air velocities are (theoretically) very small (0.004 m/sec). These conditions provide a high L/N ratio (3.0), a deliberate design decision to ensure sufficient concentrations for analysis. The cell can be used with non-planar materials by attaching an adjustable lower section (Figure 15).

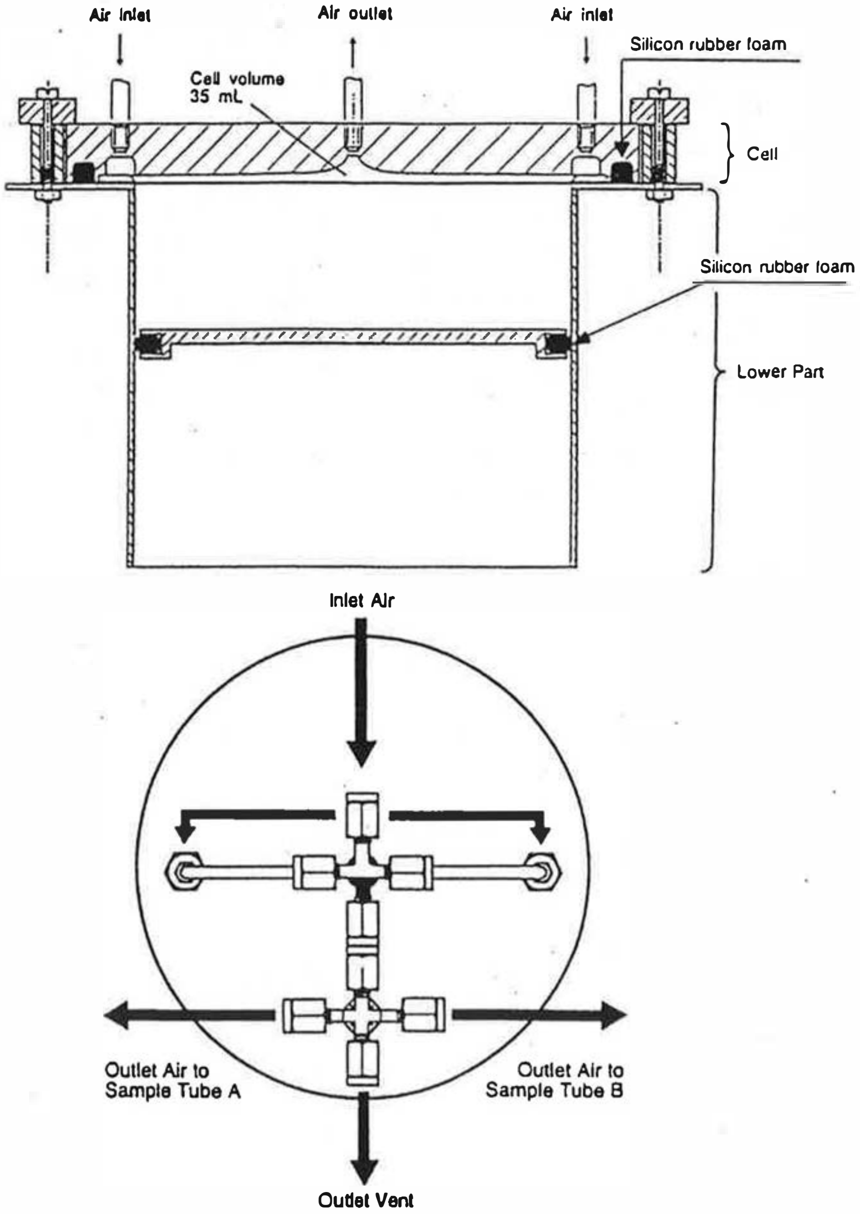

Figure 15. Field and Laboratory Emission Cell, (cell and adjustable lower part)

Wolkoff et al. (1991) compared the emission of phenol and cyclohexanone from vinyl flooring when assessed in two FLECs and two chambers operated at a similar (but unspecified) L/N ratio to FLEC. First order emission decay models were fitted to the data and model parameters of similar magnitude were found, although a lack of experimental detail and possible sample inhomogeneity limit the comparison. Gunnassen et al. (1993) evaluated VOC emission from several building materials using FLEC and small- and room-size environmental chambers. While all chambers provided the same ranking of material emissions, emission rates measured in FLEC were generally lower than found using other chambers. Clausen et al. (1993) used FLEC and small chambers to evaluate VOC diffusion-limited emission models for vinyl flooring. While similar emission decay behaviours were exhibited, different model parameters were estimated.

FLEC has become the basis for Trade standards for emission testing in Scandinavia (Gustafsson et al. 1995). Final standards have been produced for flooring materials and floor smoothing compounds and a provisional standard for paints and lacquer. The standards generally require emission flux measurements to be made after conditioning newly produced materials for 28 ± 2 days at 23°C and 50% RH. Gustafsson et al. reported TVOC emission flux values 2 to 26 weeks after application of four water-based latex paints and four industrial lacquers. Three of the latex paints exhibited zero emission fluxes, the other (an acrylic) exhibited a decreasing flux consisting mainly of 2-butoxyethanol and Texanol®. Formulation differences in the latex paints were not described. A UV curing lacquer also exhibited zero emission while the others (one water-based) exhibited 2-week emission fluxes of 400 to 1000 $\mu g/m^2.h$ that decreased to zero by 26 weeks. Emission source models were not reported. They also found equivalent measurements of formaldehyde emission flux from particleboard when assessed in FLEC and a 1 m^3 environmental chamber. The USEPA (USEPA 1994) reported comparative trials for FLEC and a 53L environmental chamber with TVOC emissions from floor wax and a latex paint. Similar emission flux decays were exhibited by both methods (Figure 16 and 17).

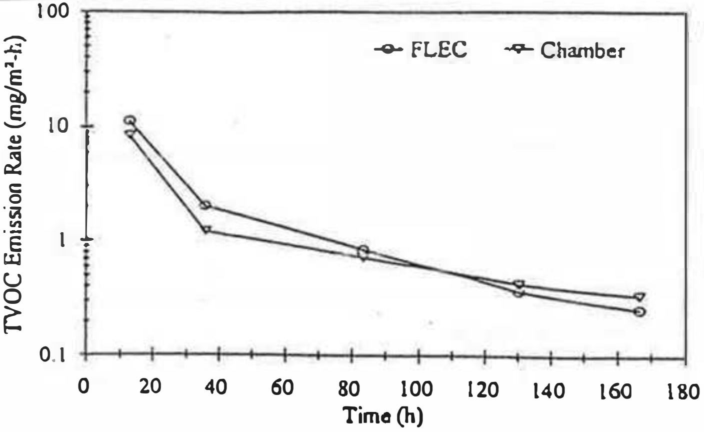

Figure 16. Comparison of FLEC and small chamber testing of floor wax (USEPA 1994).

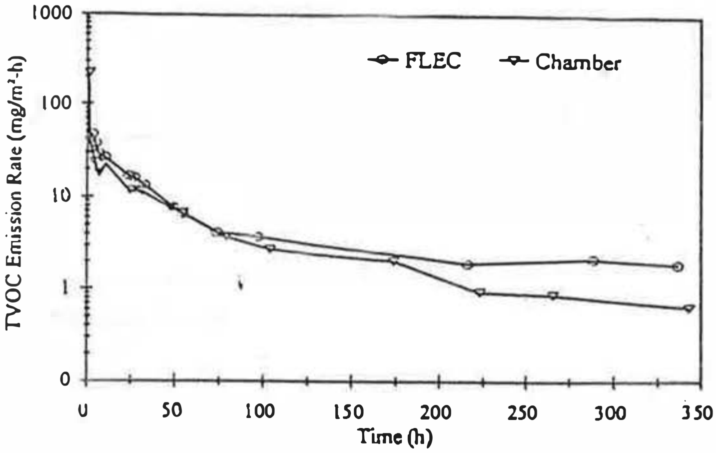

Figure 17. Comparison of FLEC and small chamber testing of latex paint (USEPA 1994).

6.1.2 Sink effects

Dunn and Tichenor (1988) proposed a differential equation to describe sink effects:

$$A\,dM/dt = k_3\,cV - k_4\,MA \qquad (63)$$

where M = mass of compound per unit area in the sink at time t
c = concentration of compound in chamber
V = chamber volume
k_3 = rate constant for loss to the sink
k_4 = rate constant for loss from the sink.

Tichenor et al. (1990) investigated the relevance of Langmuir isotherms to sink effects of both the chamber and materials placed in it. Langmuir isotherms assume a monolayer of molecules on a homogeneous surface with all adsorption sites independent and identical and no absorption into the material. Under equilibrium conditions at low concentrations:

$$k_a\,cA = k_d\,MA \qquad (64)$$

where k_a = adsorption rate constant
k_d = desorption rate constant.

If sink effects occur by Langmuir isotherms, comparison of equations (63) and (64) yields $k_3 = k_a\,(A/V)$ and $k_4 = k_d$ so that equation (63) is expressed:

$$dM/dt = k_a\,c - k_d\,M \qquad (65)$$

At equilibrium, $dM/dt = 0$ and

$$k_a/k_d = M/c \qquad (66)$$

Using a mass balance equation for compound in the chamber, they derived:

$$\frac{dc}{dt} = EF_t\,/\,V - Nc + k_a\,cL + k_d\,ML \qquad (67)$$

They experimentally investigated sink effects by introducing known amounts of pollutants (tetrachloroethylene and ethylbenzene) into the chamber supply air and measuring the rate of buildup of chamber concentration c.f. that theoretically expected. After equilibrium concentrations had been achieved, only clean air was supplied to the chamber and the rate of concentration decrease was measured (Figure 18). Data evaluation to the above equations allowed k_a and k_d to be estimated.

This experiment was carried out with the chamber empty and with a range of materials present (carpet, gypsumboard, ceiling tile, glass and upholstery). No measurable sink effect was exhibited for either pollutant by the empty chamber (electropolished stainless steel) or glass. Langmuir sorption was exhibited by the gypsumboard and ceiling tile but not by the more complex products carpet and upholstery. Significant sink effects were exhibited by the carpet sample and smaller effects by the other materials. While these findings have implications for pollutant behaviour in buildings, they also have implications for chamber experiments e.g.

where paints are evaluated on different substrates, the substrate sink effects will need to be considered.

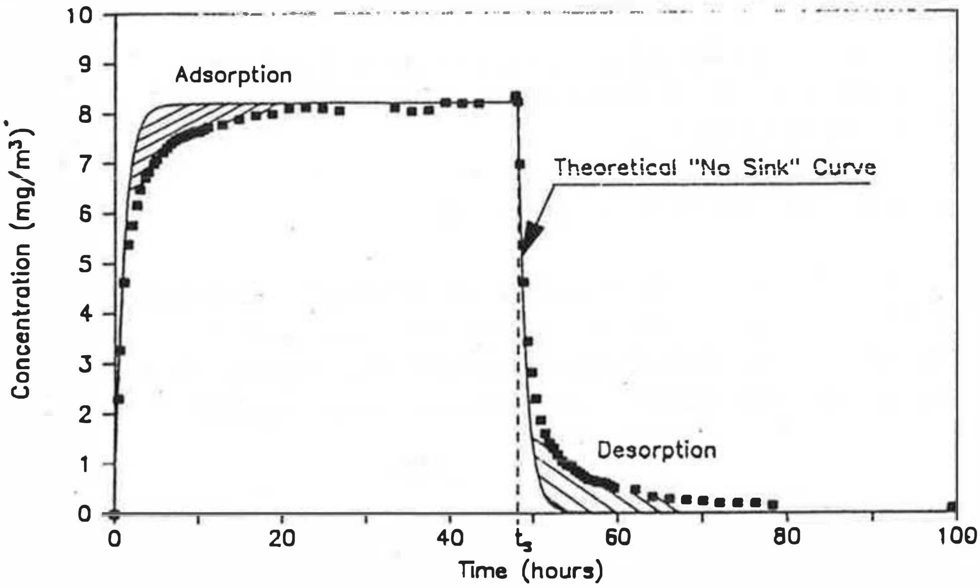

Figure 18. Chamber sink test for ethyl benzene on carpet (Tichenor et al. 1991).

Guo et al. (1990) proposed that complex materials like carpet utilise a two-box sink model that allowed for fast mass transfer processes at surfaces contacting bulk air and slow processes from surfaces within the carpet structure. This model represented the reversible sink as two boxes in series within the chamber (or room), each box having a certain volume and air exchange rate. The model was able to match the sink behaviour of ethyl benzene for a carpet for periods of 160 hours. Colombo et al. (1993) demonstrated a similar model for sorption of VOCs on carpet, gypsumboard and vinyl film, for which reversible and "irreversible" (probably very slowly reversible) sinks were included.

Levesen and Sollinger (1993) investigated the sink effect of a nylon carpet for 20 VOCs in a 1m^3 stainless steel chamber. They found sink behaviour was described by Dunn and Tichenor's Langmuir isotherm model, described by k_a and k_d, although short time periods (8 hours adsorption, desorption period unspecified) were used. They found that all compounds exhibited a sink effect with the empty chamber and a significantly greater sink effect with the carpet. In both cases the sink effect became greater as compound volatility decreased, and was especially high for n-pentadecane and 4-phenylcyclohexene. As shown by Borrazzo et al. (1993) other properties of VOCs (e.g. polarity) will also exert a very significant effect on sorption behaviour.

Jorgensen et al. (1993) investigated sink behaviour of nylon and wool carpets for α-pinene and toluene over periods of 30-40 hours and found Langmuir isotherm behaviour. The VOC concentration used, 5000 μg/m^3, was significantly higher than that of most previous studies (usually 100-200 μg/m^3).

6.1.3 Stains and non-polymeric products

Tichenor and Guo (1988, 1991) investigated VOC emission behaviour of wood stain applied to hardwood and floor wax applied to aluminium plate under different conditions of air change rate (N) and product loading rate (L). They reasoned that the emission flux should be proportional to N/L for a volatility limited source and were able to demonstrate this for the woodstain but not the floor wax. They found the latter emitted VOCs extremely fast irrespective of ventilation rate (see Section 6.1.4 for more discussion of this study).

Tichenor and Guo (1991) developed the following source model to describe the VOC emission flux (EF) of wet wood stain in chamber experiments over a 10 hour period:

$$EF = EF_o \exp(-kt) \qquad (61)$$

where EF_o = emission flux at time t=o (mass/area.time),
k = emission rate decay constant.

This implied that only wet-phase (i.e. volatility-limited) emissions were significant in the test period and that dry phase (i.e. diffusion-limited) emissions were negligible. Chang and Guo (1994) applied this source model with a first order reversible sink model to experiments in a test house where 6 m^2 of floor was coated with the wood stain. This model predicted the following concentration (C) in the test house:

$$dc/dt = -NV + (A/V)\, EF_o e^{-kt} - A_s k_a c + A_s k_d M \qquad (65)$$

where A = area of source
V = volume of house
A_s = sink area in house
M = mass of VOC in sink at time t
($dM/dt = k_a c - k_d M$)
k_a, k_d = adsorption and desorption rate constants for sink.

The empirical parameters – EF_o, k, k_a, k_d – were estimated to fit this equation to concentrations of nonane, decane and undecane in the test house. Sink effects in the house were high and significantly prolonged the occurrence of elevated VOC concentrations in the house compared to concentrations predicted for no sinks. A direct inverse relationship was observed between sink strength (k_a/k_d) in the house and alkane volatility. Chang and Guo reasoned that if volatility-limited processes were controlling wood stain organic emissions to the indoor air, then there should be a one-to-one relationship between relative values of k for each alkane and their relative vapour pressures. This relationship was observed.

Chang and Guo (1992) reported on the emission performance and modelling of a timber floor wax. This was assessed immediately after wax application to aluminium plate in a 166 L stainless steel chamber and with application to the floor of a test house. Chamber concentrations (c) of 11 major VOCs were found to decrease at the same rates with time according to:

$$c = c_o \exp(-Nt) \qquad (68)$$

where c_o = chamber concentration at time t = 0, and
N = effective air change rate (averaged for 11 compounds).

Assuming first order emission flux decay they derived that for fast decaying (high k) sources:

$$c_o = \frac{EF_o \cdot A}{k \cdot V} \tag{69}$$

This meant that for this fast decaying source, the initial chamber concentration C_o was approximated by the initial mass of VOC in the source divided by the chamber volume. Physically, an initial pulse of VOC emission occurred as the chamber was loaded. Thereafter, the emission rate of the floor wax decayed to a negligible level and the VOCs present in the chamber were diluted according to the chamber air change rate. Chang and Guo applied this source model to VOC concentrations in a test house where 6 m^2 of floor was coated with the wax. By including sink adsorption and desorption processes in the house model and deriving empirical rate constants for these processes, they were able to closely predict measured VOC concentrations over a 50 hour period.

6.1.4 Paints and coatings

Tichenor (1987) showed that the emission factors of wet materials such as caulking compound and floor wax decreased significantly (by orders of magnitude) within several hours of application. He also demonstrated that a "sink" effect occurred with chamber walls, influencing the chamber concentrations and emission factor decay rate. Sanchez et al. (1987) reported decreasing rates of VOC emissions with time of drying of floor adhesives. In a companion paper, Dunn (1987) explored models for small chamber emission dynamics for an acrylic latex film and showed that a predictive model needed to allow for temporary retention of VOCs by chamber walls, i.e. a "sink" effect.

Tichenor and Guo (1988) investigated the effects of air change rate (N) and product loading (L) on the emission flux dynamics of three wet sources: woodstain and polyurethane lacquer applied to hardwood boards and floor wax applied to aluminium plate. Small chamber testing commenced shortly after the coatings were applied and continued for 10-24 hours. Experiments were carried out at a range of ventilation rates (0.3 to 4.6 hr^{-1}) and loading ratios (0.06 to 1.3 m^2/m^3). They applied a model to chamber air concentrations which assumed the chamber was a continuous stirred tank reactor and that emission flux changed with time by a first order decay curve such as equation (61) (Dunn and Tichenor 1988). This model was found to fit all data sets and allowed source emission constants EF_o and k to be calculated for each experimental condition, as presented in Table 3.

Table 3. TVOC emission model parameters for wet source materials (Tichenor & Guo 1988)

Test No.	Material	N (h^{-1})	L (m^2/m^3)	N/L	EF_o mg/m^2k	k (h^{-1})	EF_o/k (mg/m^2)
1	wood stain	0.35	1.3	0.3	2,200	0.24	9,200
2		0.35	0.1	3.5	21,000	1.5	14,000
3		2.5	0.7	3.6	17,000	1.2	14,000
4		4.6	1.3	3.5	27,000	2.4	11,000
5	polyurethane	0.5	0.21	2.4	1,700	0.25	6,700
6		1.0	0.42	2.4	2,600	0.29	9,000
7		1.0	0.21	4.8	6,500	0.61	11,000
8		2.0	0.21	9.5	5,800	0.64	9,500
9	floor wax	0.25	0.12	2.1	38,000	6.3	6,000
10		0.5	0.12	4.2	23,000	5.3	4,300
11		0.5	0.06	8.3	19,000	5.4	3,500
12		1.0	0.12	8.3	28,000	10.2	2,800
13		2.0	0.24	8.3	32,000	8.1	4,000
14		2.0	0.12	16.7	23,000	6.3	3,700

Tichenor and Guo reasoned that for a volatility-limited source, increasing ventilation rate (N) would increase emission flux while increasing loading ratio (L) would decrease emission flux. Thus emission flux should be similar for experiments with the same N/L values and lower for experiments with low N/L values. Results for the wood stain comply with this behaviour e.g. tests 2, 3, and 4 resulted in similar EF_o and k values while test 1 resulted in much lower EF_o and k values, even though the total quantities emitted (source strength, EF_o/k) were similar in all four experiments. Vapour pressure suppression in test 1 was considered to result in the much lower initial emission flux and much slower decay. This suppression also appeared to occur for the polyurethane lacquer at low N/L (test 5). However emission flux at high N/L values (test 7 and 8) were similar indicating diffusion limiting processes may have occurred; this is consistent with the polymeric nature of the polyurethane film c.f. the non-polymeric wood stain. The results for the floor wax showed little relationship to N/L values but this material emitted extremely fast (as shown by k), much of the VOC being emitted in the first few minutes of test, preventing any influence of chamber ventilation on the emission process.

Gunnarsen et al. (1993) reported Texanol emission flux measurements in several types of chambers for an aged (~3 weeks) acrylic latex paint. Measurements ranged from 0.36 to 2900 $\mu g/m^2.h$. He proposed that the "specific ventilation rate" (V′, air supply rate per sample area) was a suitable factor to evaluate the influence of ventilation on product emission flux. By combining data from the different chambers he demonstrated that the following relationship described this influence:

$$EF = k_a\,[1 - \exp(-k_b\,V')] \qquad (70)$$

where k_a and k_b were constants.

He concluded that there was an increase in EF as ventilation increased at low ventilation levels since evaporation was volatility-limited. At high ventilation levels there was little influence of ventilation on EF since solid diffusion processes were limiting. It seems unlikely that volatility-limited processes would occur 3 weeks after film formation, as discussed in Section 5. The findings may have been associated with other factors, e.g. emission data generated by the three different types of chamber may not have been directly comparable.

Vokl et al. (1990) reported emission tests for a polyurethane lacquer and an alkyl paint applied to pine board. Tests were conducted in a 216 L stainless steel/glass unstirred chamber at low ventilation rates (0.04 to 0.5 ACH) and loading rates of 0.4 and 0.25 m^2/m^3, respectively. Coatings were dried for 40 hours before sampling commenced. Interpretation of the findings is hindered by the lack of experimental detail and presentation of data as emission flux rates.

Colombo et al. (1990) reported an emission test for a polyurethane lacquer on plywood in a well-stirred 450 L glass chamber. The objective was to measure the steady-state emission rates of the major VOCs at 23°C, 45% RH and 0.25 ACH. The sample had been prepared and dried 2-4 months previously and sealed in aluminium foil. Trials showed that total VOC emission flux decreased to "steady state" levels (defined as $\leq$ 10% concentration change per day) in 65 days and so emission fluxes ($\mu g/m^2.h$) for VOCs were determined at this time, e.g. n-dodecane 13.0, hexanol 120, n-undecane 97, pentanal 36, n-tridecane 28, n-decane 21, propanal 14. Interestingly, the authors attributed the above aldehydes to the lacquer rather than the plywood. Formaldehyde emission flux from the latter was considerably lower at only 6 $\mu g/m^2.h$.

Gehrig et al. (1993) measured the emissions from low solvent (1.5%) paint, assumed to be water-based, in a 1 m^3 chamber over a 4 day period (commencing 30 minutes after paint was applied). The paint was applied to glass, paper-faced gypsumboard or a wood-chip wall paper. The major VOCs emitted were nonane, decane, undecane, trimethyl benzenes, butyldiglycol and butyldiglycol acetate. Emission dynamics and mechanisms were not quantified although most of the emissions occurred within the first 12 hours of test. Alkane emission behaviours were the same for all substrates but emissions of the polar VOCs were less for the porous substrates, due to unspecified mechanisms.

The first order emission decay model (equation 61) has shown consistency with emission data for wet and previously wet sources, including paints, as described by studies already reviewed. However since paints and coatings consist of polymeric films, different source models should be applicable to the initial "wet phase" evaporation (e.g. equation 61) and the subsequent slow "dry phase" evaporation. Clausen et al. (1990, 1993) proposed that separate models incorporating film thickness (ℓ) effects were applicable to these phases:

$$EF = (M_o\, k_v / \ell)\, e^{-(k_v/\ell)t} \qquad \text{volatility-limited phase} \tag{71}$$

$$EF = (M_o\, k_d / \ell^2)\, e^{-(k_d/\ell^2)t} \qquad \text{diffusion-limited phase} \tag{72}$$

where M_o = mass of VOC in source ($\mu g/m^2$) at time t=o
k_v = rate constant for volatility-limited evaporation for $\ell = 1\mu m$ ($\mu m.h^{-1}$)
k_d = rate constant for diffusion-limited evaporation for $\ell = 1\mu m$ ($\mu m^2.h^{-1}$).

Note that for a specific film thickness, the form of these equations is identical to equation (61).

Clausen (1993) investigated the emission of three high boiling VOCs from a water-based interior paint applied at thicknesses 20µm, 28µm and 56µm and predried for 24 hours. Using a chamber-sink effect model he estimated the following rate constants (Table 4).

Table 4. Estimated first order emission decay parameters for VOCs emitted over 2 weeks from a waterborne paint at three thicknesses (Clausen 1993).

VOC	Ave dry film thickness (µm)	k h^{-1}	k_v $\mu m.h^{-1}$	k_d $\mu m^2.h^{-1}$	M_o $mg.m^{-2}$
Propanediol	22	0.025	0.56	12	4.6
	28	0.057	1.6	44	3.9
	56	0.036	2.0	114	68
Butoxyethoxyethanol	22	0.018	0.40	8.7	2.4
	28	0.020	0.55	15	3.2
	56	0.009	0.49	28	68
Texanol	22	0.015	0.33	7	35
	28	0.016	0.46	13	46
	56	0.005	0.27	15	410

Clausen applied the paint by roller and found this resulted in very uneven films. Multiple thickness measurements on each specimen exhibited relative standard deviations of ± 30 to 55% and poor correlation between M_o and film thickness is evident for each VOC. Within this limitation the rate constants are more consistent with a volatility-limited than a diffusion-limited process.

Clausen et al. (1993) considered the role of internal diffusion on VOC emissions for vinyl flooring in an approach which may have relevance to late-stage drying of paints and coatings. Using Fick's first law and the observed exponential dependence of the diffusion coefficient on VOC concentration in the material (see equations 20 and 22) they derived an equation for the diffusion-limited flux (F) from sources above a specific thickness:

$$F = [K/\ell)t + F_o^{-1}]^{-1} \tag{73}$$

where F_o = flux at time t = o
K = exponential proportionality constant for concentration dependence of diffusivity
ℓ = thickness of the source.

This model shows that the emission flux may be approximately proportional to 1/t when F is large and a stable concentration gradient has been established in the material. They were able to show a fit of this model to VOC (phenol, cyclohexanone) emissions from a vinyl flooring assessed in FLEC and two environmental chambers. However different estimates of K/ℓ and F_o were found with each chamber for unknown reasons. Also the first order exponential emission model could fit the emissions (although parameters were not responsive to the different ventilation conditions, suggesting control by internal diffusion). Jensen et al. (1993) found this Clausen's et al.'s model could fit VOC emissions from linoleum from 24 to 1000 hours, the fit being better than the first order exponential decay model. By contrast, Bremer et al. (1993) found the latter provided good fit for VOC emissions from vinyl flooring.

Christiansson et al. (1993) modelled diffusion limited emission of VOCs from PVC flooring by assuming a constant film diffusion coefficient D and one-sided emission, for which a simplification of general diffusion equations (Crank and Park 1968, Vergnaud 1991) yielded two equations relevant to initial and final depletion of the source:

$$\frac{M_t}{M_\infty} = \frac{2}{\pi^{1/2}} \left(\frac{Dt}{\ell^2}\right)^{1/2} \qquad \text{for } \frac{M_t}{M_\infty} \leq 0.5 \qquad (74)\ (\text{also } 34)$$

$$\frac{M_t}{M_\infty} = 1 - \frac{8}{\pi^2} \exp\left(-\frac{D\pi^2 t}{4\ell^2}\right) \qquad \text{for } \frac{M_t}{M_\infty} \geq 0.55 \qquad (75)$$

where M_t = mass emitted to air at time t
M_∞ = total emittable VOC is the material
ℓ = thickness of the plane material.

The initial stage will involve an emission flux that is inversely proportional to time$^{1/2}$:

$$\frac{dM_t}{dt} = \frac{A C_o}{\pi^{1/2}} \left(\frac{D}{t}\right)^{1/2} \qquad \text{for } \frac{M_t}{M_\infty} \leq 0.5 \qquad (76)$$

while the final stage will involve an emission flux that reduces exponentially with time:

$$\frac{dM_t}{dt} = \frac{2 A C_o D}{\ell} \exp\left(-\frac{D\pi^2 t}{4\ell^2}\right) \qquad \text{for } \frac{M_t}{M_\infty} \geq 0.55 \qquad (77)$$

where A = area of material exposed to air
C_o = initial (homogeneous) concentration of VOC in material.

Christransson used these equations to calculate room concentrations of VOCs emitted from vinyl flooring over a one year period but provided no actual measurements by which to assess the validity of the model.

Tichenor (1995) described the USEPAs research plan for determining VOC emissions data for indoor sources and its specific application to latex paints as:

stage 1: small chamber source characterisation
stage 2: IAQ modelling based on source characterisation
stage 3: test house validation of models

Previously this approach had been used to evaluate VOC emissions from dry-cleaned clothing (Tichenor et al. 1988) and from wood finishing products (Chang and Guo 1992, 1993, 1994). Tichenor described the research on latex paints which had progressed to stages 1 & 2. A polyvinylacetate latex paint with an organic volatiles content of 45 mg/g was assessed in a 53L environmental chamber. Freshly painted (2-3 minutes) substrates of stainless steel or gypsumboard were evaluated for 7 days. Emissions fluxes from painted gypsumboard were considerably lower due to undetermined sorbency properties (e.g. adsorption, absorption) and this substrate was adopted for further experiments. In a long term (6 month) experiment, most VOCs (propyleneglycol, butoxyethoxyethanol, Texanol®) decayed to near quantitation limits after 2-3 months, while ethylene glycol persisted at levels 15-20 times higher. It was found that a first order decay source model could not be fitted to TVOC emissions after 7 days, while a gas-phase mass transfer model could be fit to the results (Figure 19). However neither of these models could fit long-term measurements, whereas the following second order model could do so (Figure 20):

$$EF = (EF_o)/(1 + k_2 (EF_o) t) \tag{78}$$

This was considered to indicate that long term emissions were controlled by VOC diffusion processes that occurred in the gypsumboard.

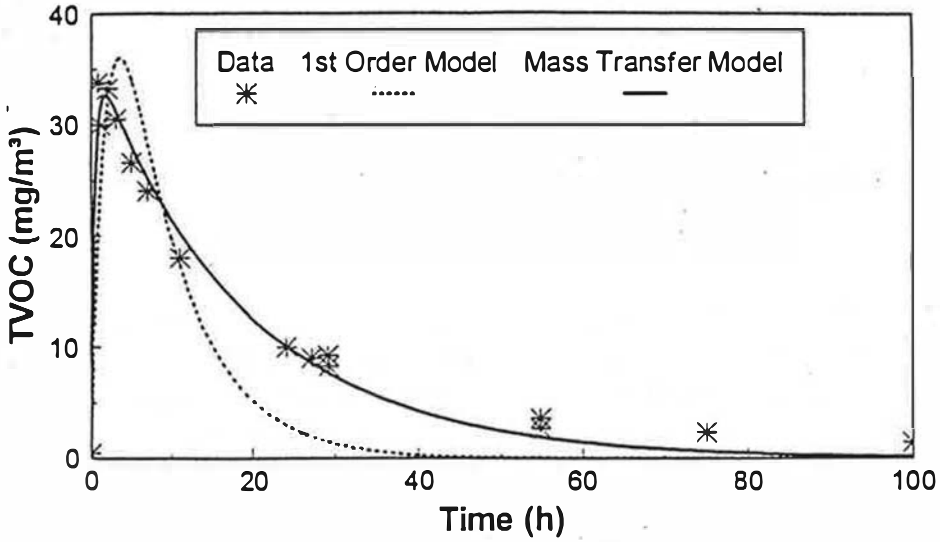

Figure 19. Short-term emission models for PVAc latex paint on gypsumboard (Tichenor 1995).

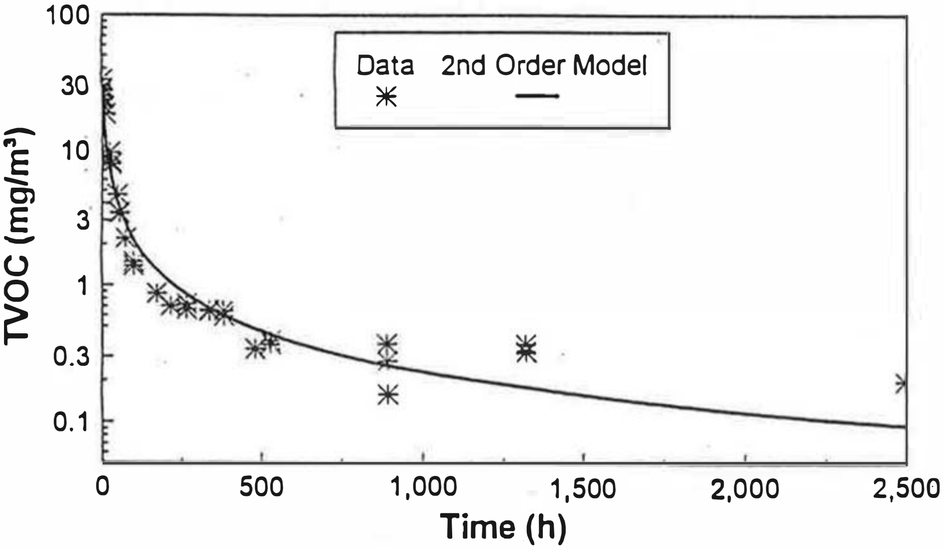

Figure 20. Long-term TVOC emission model for PVAc latex paint on gypsumboard (Tichenor 1995).

6.2 Full Scale Emission Studies and Models

6.2.1 Modelling of indoor air concentrations

A major aim of measuring VOC emission dynamics in chamber experiments is to provide emission flux data for use in models that predict indoor air concentrations for "typical" buildings. Chamber emission tests tend to be designed to simulate these "typical" environments and to provide emission flux-time data relevant for determining occupant exposures. With a link established between source emission flux and indoor air concentrations, it should be possible to predict emission flux limits to maintain indoor air concentrations below "goal" concentrations, an approach with limited application to date (Tucker 1991, Black et al. 1993), and which will be discussed later (Section 7.2).

Critical to this approach will be:

(a) how the chamber emission measurements are modelled so that correct emission flux dynamics data are derived,

(b) how indoor air is modelled when using the chamber data.

Most USEPA studies have used similar mass balance models, with or without sink corrections, for analysing chamber measurements and for predicting indoor air concentrations. This approach has worked reasonably well for emissions from drycleaned clothing (Tichenor et al. 1988), floor wax and timber stains (Chang and Guo 1992, 1994) and tile adhesives (Nagda et al. 1995). Indoor air models in these cases are not generally fully predictive since they assume interzone airflows and sink parameters to force the model to fit air concentration measurements over time. Sparks et al. (1993) describe the USEPA's model EXPOSURE for predicting indoor air pollutant concentrations and occupant exposure to pollutants which has generally been applied with a first order emission decay source and Langmuir-type sink adsorption and desorption rate constants.

Colombo et al. (1990) described an empirical model for characterising chamber VOC concentrations which, while general in its application to sources of different types of behaviour, was applied irrespective of sink concerns. Their general source model was:

$$c = (A(1 - e^{-Bt}) - C\,(1 - e^{Dt}) \qquad (79)$$

where A and C are linear coefficients and B and D are rate coefficients. For a decaying flux source this simplified to:

$$c = A(e^{-Dt} - e^{Bt}) \qquad (80)$$

and for a constant emission flux source:

$$c = A\,(1 - e^{-Bt}) \qquad (81)$$

This source model has not been used to predict indoor air concentrations and will be limited for such applications since it is a purely empirical model with no consideration of the physical processes (such as dynamic emission rate) involved in VOC emission. However for fastemitting wet sources Colombo and DeBortoli (1992) showed it was generally equivalent to physical models in accurate estimation of chamber emission rates.

Tichenor et al. (1993) noted that empirical and semi-empirical models were limited by (a) not providing a physical description of the emission process, and (b) not separating the parameters describing the source from those describing the environment. They developed a fundamental mass transfer model for VOC emissions from coatings based on a volatility-limited process. The model assumed that all mass transfer was by molecular diffusion across a laminar boundary layer at the source/air interface, so that by Ficks law:

$$EF = (d/\delta)\,(c_s - c) \qquad (82)$$

where d = molecular vapour diffusivity (m^2/h)
δ = boundary layer thickness
c = VOC concentration in the bulk air
c_s = VOC vapour concentration at the source surface.

Assuming that (a) the equilibrium VOC vapour pressure c_v for a wet coating was independent of the coating thickness (which they verified), (b) $c_s = c_v\,(M_t/M_o)$ where M_t = mass of VOC in the coating at time t, and (c) the average vapour diffusivity d approximates that of the most abundant compound, it was derived that:

$$EF = \{c_v\, d/[\delta(r_1 - r_2)]\}\ [(r_1 + N)\exp(r_1 t) - (r_2 + N)\exp(r_2 t)] \qquad (83)$$

where N = chamber air change rate

$$r_{1,2} = 0.5\ \{-[N + Ld/\delta + d\,c_v/(\delta\, M_o)] \pm [(N + Ld/\delta + d\,c_v/(\delta M_o))^2 - 4d\,N\,c_v/(\delta M_o)]^{1/2}\} \qquad (84)$$

L = product loading rate = A/V = source area/chamber volume.

They applied this model to several wet sources: floor wax, wood stain, polyurethane coating. Four model parameters: M_o, c_v, d and A were properties of the source. c_v was determined by static headspace measurements on each source, d from tabulated diffusivities, and M_o from source analysis. Three model parameters: V, N and δ were properties of the environment. Only δ was unknown. Small chamber emission testing of woodstain allowed (d/δ) to be estimated and thereby δ was determined to be 24 ± 4 mm. The model was found to fit small chamber VOC emission measurements for the drying of woodstain and floor wax but only for the initial drying (~ 15 hours) of a polyurethane lacquer applied to oak. A first order emission decay model provided a somewhat worse fit to the chamber measurements. While not discussed by Tichenor et al., it is assumed that film diffusion effects predominated in the late-stage drying of the polyurethane coating, limiting the application of the volatility-limited model. Tichenor et al. characterised the mass-transfer model parameters for a test house in which the same wet sources were applied and, by incorporating a sink mass balance model, were able to predict indoor VOC concentrations up to 25 hours after product application.

Inherent problems in indoor air modelling based on small chamber emission measurements and validation of models were discussed by Guo (1993). These included poor understanding of physical conditions in small chambers (particularly air velocity and turbulence) relative to indoor air conditions, and the limited periods over which some models may apply. Salthammer (1996) showed that statistical limitations of chamber emission data can limit the assignment of the correct source emission model. A further inadequacy is the effect of VOC back-pressure on the emission rate modelling in small chambers and buildings. Jaycock (1994) predicted by modelling that backpressure became important for a volatilising source in a typical room at high loading ratios (e.g. L ~ 0.3 m^2/m^3). Under these conditions, ventilation rate had little relative influence on equilibrium room concentrations. For small sources (L ~ 0.00004 m^2/m^3) backpressure was essentially zero and equilibrium concentrations were inversely proportional to ventilation rate. Since interior coatings must generally entail a high loading ratio, this factor must be accounted for (e.g. as it is in the model of Tichenor et al. (1993)).

Lastly, it is clear from boundary layer vapour diffusion theory that surface air velocity (and turbulence) will be critical to VOC emission flux from volatility-limited sources. Gunnarsen (1991) derived Figure 21 to describe relative rates of mass transfer from a flat volatilising surface. Surface air velocities within this range do occur in buildings, e.g. high velocities near air inlet diffusers. The derivation indicated that poorly controlled air velocity could affect measured VOC emission flux several-fold. Better control of surface air velocities has been proposed for chamber experiments (Zhang et al. 1993).

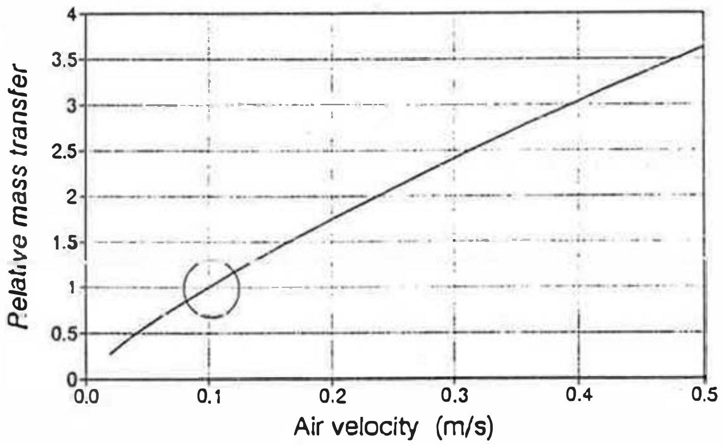

Figure 21. Relation between relative mass transfer rate and air velocity when only evaporation is limiting the mass transfer (Gunnarsen 1991).

6.2.2 Full-scale emission studies

These studies differ from small chamber studies in that the application phase for coatings may be included in measurements and scale-up problems are likely to be less severe. The studies have been made in room-size environmental chambers with good environmental controls and in actual buildings with poorer control and the need for site characterisation in each case.

6.2.2.1 room-size chamber studies

Smith et al. (1987) described a 34 m^3 ventilated chamber lined with gypsumboard for assessing exposure to VOCs during the application of wet products for short periods (~50 hours) after application. Emissions from application of an interior acrylic latex paint containing 1.3% w/w diethylene glycol monobutyl ether (DGME) were measured. The process was not physically modelled. Instead, the personal (breathing zone) exposure of the applicator to DGME was measured and compared to concentrations measured in the chamber. No difference in average concentrations was found in comparing personal to area concentration measurements, and the maximum DGME concentration observed was 0.52 ppm during the application period and this decayed to 0.07 ppm by 54 hours after application (conditions unspecified).

Wallace et al. (1987) described VOC emissions from a range of building materials in a 34 m^3 aluminium chamber with a linear air flow from floor to ceiling. Test conditions were 25.0 to 26.5°C, 60 to 75% RH, 0.60 ACH, and samples consisted of eleven 2.0 m x 1.2 m panels placed in the chamber for not less than 12 hours before air sampling. These conditions were arbitrarily chosen and equilibrium concentrations may not have been achieved in the chamber. In one experiment, a white undercoat paint applied to gypsumboard was assessed one-week after application to yield the following emission fluxes ($\mu g/m^2h$): 1,1,1 trichloroethane 1.9, benzene 7.2, n-decane 14, n-undecane 90.

6.2.2.2 room experiments

Several experiments have been carried out in typical rooms of field buildings. These have generally focussed on VOC emissions and occupational exposure during the application of paints and coatings and may not provide much attention to indoor air exposures.

Hansen (1987) investigated breathing zone and room concentrations of VOCs during the application of a range of wet products in various rooms. He proposed a model for pollutant flow into and out of the room as:

$$V \frac{dc}{dt} = - k\, q\, c + (EF) \tag{85}$$

where V = room volume
c = VOC concentration in air
q = volumetric air flow rate from room
k = factor allowing for inefficient mixing of room air

which was solved as:

$$c = \frac{(EF)}{k\, q}\left(1 - e^{-(k/V)qt}\right) \tag{86}$$

Hansen assumed EF was identical to the evaporation rate for the neat solvents that were used in the products (paint remover, glue, solvent-based paint and lacquer). He found he could calculate room concentrations within 1.0 to 1.5 times measured concentrations when applying a fair amount of product (~ 150 mL) in a fairly small room (~ 35m^3). For small amounts of product and large rooms the factor was 1.5 to 4.0 since for these situations k was expected to be well below the assumed value of 1.

Miller et al. (1990) described experiments in a 28 m^3 office in which different areas (2 to 10 m^2) of board were coated by roller with a solvent-based paint at a range of ventilation rates (0.1 to 20 ACH). The aim was to determine how quickly and under what conditions occupational exposure standards were exceeded. As expected, ventilation rates and area coated were critical factors but the absence of physical modelling of the experiments limited their understanding and application to other conditions. Brown et al. (1990) compared wet-stage VOC emissions from a similar paint when used to paint the walls of a 44 m^3 room (ventilated 5 ACH, loading ratio 0.95 m^2/m^3) and when assessed in a ventilated desiccator (ventilated 8.6 ACH, loading ratio 4.3 m^2/m^3). The findings were limited by a lack of physical interpretation of processes and the evaluation of only one paint.

Grourke et al. (1993) described experiments in which acrylic latex paints were applied by airless spray in either a 20.7 m^3 low-infiltration room (ventilation ~ 0.06 ACH) or a 18.5 m^3 room of a house (ventilation 0.3 – 1.2 ACH with door open, 6–7 ACH with door and window open). Airless spray application was used since preliminary trials showed it generated two- to three-times the levels of volatiles that brush application generated. Room concentrations of monomers, solvents and additives were compared to occupational exposure standards, none of which were exceeded except for the mildewicide at the lowest ventilation rate.

Two studies have considered the physical processes occurring during paint application and developed models to describe these processes that allow different practical situations to be assessed. Bjerre (1989) described the "painters exposure model" MEM1 which assumed constant emission flux, no sink losses, complete mixing of room air, negligible back-pressure and specific application and drying-times for the process. Interactions of the latter times meant four models were possible, each with different outcomes for the rate of application and drying, the area coated, the ventilation rate and the solvent content. The models were characterised as:

case 1 – evaporation-limited with quadratic build-up,
case 2 – mass-limited with linear build-up,
case 3 – evaporation-limited with linear build-up, and
case 4 – mass-limited steady state.

where quadratic, linear and steady state referred to the way exposure load depended on area coated and thereby the application time. Bjerre applied the model to data from previous investigations of painters' exposure in chambers and found good correlation.

Zeh et al. (1994) considered exposure of painters to VOCs (boiling points < 200°C) from latex paints and plasters. Their model was specific only to "wet" stage exposure, prior to film formation, and used similar assumptions to Bjerre (1989). For the time period between the start and end of paint application, they derived:

$$m_t = \{[1 - \exp(Bt)]/B - [1 - \exp(Nt)]/N\} \, v_p \, \ell \, C \exp(-Nt) \qquad (87)$$

$$\text{with } B = N - k_1/\ell$$

where m_t = mass of VOC in indoor air at time t
N = air change rate (ℓ^{-1})
k_1 = evaporation constant (cm h^{-1})
v_p = paint application rate (m^2 h^{-1})
ℓ = coating thickness
C = VOC concentration in coating

After application:

$$m_t = \{(k_1 M_{we}/ \ell)\,[\exp(B(t-t_e))-1]/B + m_e\}\ \Sigma\exp(-k_2(t-t_e)) \qquad (87)$$

where M_{we} = mass of VOC on wall at end of application
t_e = time to end of application
m_e = m_t at end of application.

Zeh et al. determined values of k_1 for five water-based latex paints and plasters by measuring the VOC content of cast films as they dried under standard conditions (23°C, 50% RH). These were applied to the walls of two typical room (volumes $41 m^3$ and $47\ m^3$) operated at ventilation rates of 0.5 to ~ 40 ACH. The model was able to calculate VOC concentrations during application and for a short (~20 min) post-application period, after which calculated and measured concentrations increasingly diverged, probably as the evaporation mechanism switched to a film diffusion-limited process.

Zeh et al. applied the model to evaluate a range of factors influencing VOC concentrations during application of latex coatings. Critical factors were ventilation rate greater than 1 ACH, room volume, VOC content, and the way application time was distributed over the work period.

6.2.3 Building experiments

Under some circumstances VOC measurements in buildings have been used to estimate source emission fluxes. Estimation requires knowledge of source area, emission kinetics, installation time, background VOCs, ventilation rate and efficiency, sink adsorption and desorption rate constants etc. Sink factors are difficult to predict although USEPA test house IAQ modelling based on Langmuir isotherms have provided estimates for some compounds (Chang and Guo 1992, 1994, Tichenor 1995) supported by small chamber sink trials (Tichenor et al. 1991, Jorgensen et al. 1993, Levesen and Sollinger 1993, Colombo et al. 1993).

Kerr (1993) ignored sink effects when estimating VOC emission flux from new carpet and adhesive in a large office building. He assumed that the steady-state indoor air VOC concentration (c_{ss}) would be related to EF by:

$$EF = \frac{V}{AN} c_{ss} \qquad (89)$$

where V = volume of floor level carpeted
A = area carpeted
N = air change rate.

Since building concentrations were found to decrease exponentially, he estimated the EF of TVOC at 1 day to be 104 mg/m^2.h.

Haghighat et al. (1994) carried out a numerical study to predict VOC concentrations in a newly painted, partitioned office and to assess the effects of ventilation rate and partition layout. They modelled a displacement ventilation system with the volatility-limited mass transfer model of Tichenor et al. (1993). They predicted that peak concentrations would be reached 3-4 hours after paint application and that they would be higher and decay more slowly when partitions contacted walls rather than being centrally positioned in the office.

Hodgson and Girman (1989) measured VOC concentrations in two new buildings approximately five months after interior finishing. Indoor pollutant source strengths for VOCs (S $\mu g\ h^{-1}$) were estimated from a mass balance model which assumed perfect mixing in the building, no VOC removal other them by ventilation and no loss of outdoor air VOCs as they were transported into the building:

$$S = VN \frac{c_t - c_o e^{-Nt}}{1 - e^{-Nt}} - VN\, c_{od} \qquad (90)$$

where V = building volume
N = air change rate
c_t = indoor VOC concentration at time t
c_{od} = outdoor VOC concentration.

The authors used specific source strength (S/V) to assist in comparison of different buildings. Comparison by this measure must consider the expected low precision in thc source estimate.

7. CLASSIFICATION OF EMISSION PERFORMANCE

7.1 Low Emission Coatings

An international push for low VOC paints and coatings exists because of the vast quantities of VOCs that these products release to the atmosphere. For example, a conservative estimate of the VOC release from paints in Europe in 1990 was 700,000 tonnes (Willemse 1993). In the US, surface coatings release approximately 19 per cent of stationary area source VOC emissions (Northeim and Darden 1993). VOC limits for paints and coatings have been established in some countries, eg. for decorative paints 250 g/L (Strametz 1992) and the paint industry has responded by a range of new technologies (Willemse 1993). Coatings used in building and construction constituted 51% of the worldwide consumption in 1990 (23 million tonnes) (Strametz 1992) and so a significant impact of these changes on indoor paint emissions is likely.

The typical VOC content of interior water-based latex paints is 180 g/L although in 1992 some products with VOC < 12 g/L were introduced (Wicks et al 1992). VOCs in typical latex paints act as cosolvents and coalescing solvents, essential components to paint drying and film formation. Modification to the polymer latex (eg. using a low Tg resin that crosslinks and hardens after coalescence or is highly pigmented) is one factor allowing VOC reduction in latex paints (Broek 1993). Production of latex polymers with low residual VOCs is another factor (Aviles et al 1990).

Gloss enamel paints are usually alkyd solutions in solvents and require VOC contents greater than 275 g/L to be functional. However alkyd enamels with VOC contents of 155 g/L which retain good film properties have been produced by using reactive diluents which coreact with the alkyds (Lakin 1982, Wicks et al 1992).

While limits on VOC contents are directed at lowering ambient VOC emissions from coatings, they are oversimplistic in approach since other health and environmental issues have been ignored. For example, the low VOC coatings may use more hazardous VOCs and create health problems, or they may be inferior products (Gill 1993) requiring greater maintenance costs and use of resources. Weitz and Warren (in Northein and Darden 1994) describe life cycle analysis (LCA) techniques to assess alternative coatings and to better account for the health and environmental impacts of new materials. While beyond the scope of this report, it is clear that new low–VOC coatings (whether for improvement of outdoor or indoor air) should be assessed by LCA techniques rather than be prescribed by a VOC content or emission flux. However this approach has not been used to date for low–emission coatings.

Low– or no–VOC interior decorative paints are of comparatively recent origin, although in many countries there has been a gradual shift in usage from solvent–based to water–based paints over the last 15 years. While typical water–based paints are much lower in VOC content than typical solvent–based coatings, the former are not considered low–VOC products in this discussion. This is reasonable since typical water–based latex coatings contain approximately 10% by weight of volatile organics.

Broek (1993) discussed technical aspects of formulating low–VOC water–based latex coatings. These were:

(a) reduction of odorous monomer residues in the latex polymer (eg. previous levels of 0.3–0.5% vinylacetate can now be as low as 0.01%),

(b) reduction of ammonia needed to stabilise the latex,

(c) inclusion of crosslinking agents or modification to latex particle morphology in place of high Tg resins with coalescing solvents,

(d) more effective coalescing solvents and less toxic additives (thickness, defoamers, biocides, etc).

He noted that while solvent–free wall paints were available, it was difficult to develop a waterborne semigloss paint for wood (brush quality) containing less than 8% of solvents or coalescents without losing technical performance. Aviles et al. (1990) described research to develop zero VOC semigloss water–based latex paints using newly developed binders that required no coalescent. Tuckerman and Maurer (Northeim and Darden 1994) described development of such a product to commercial production. Use of a novel latex and additives free of solvents were factors in product development.

7.2 Emission Limit Specifications

Tucker (1990) and Black et al (1993) described emission limit specifications applied to interior construction and finishing materials and furniture used in USEPA and State of Washington buildings. Both organisations required chamber emission testing of products to be used with indoor air modelling of the buildings to ensure that products did not contribute TVOC concentrations above 500 μg/m^3 (within 30 days for State of Washington requirement). The State of Washington also required disclosure of the presence of carcinogens and teratogens and emission testing with modelling to ensure:

(a) 4 phenylcyclohexene and formaldehyde concentrations not exceeding 1 ppb and 50 ppb, respectively, within 30 days of installation,

(b) no other pollutant concentration exceeded 10% of occupational exposure standards.

Tucker recommended the following default values (Table 5) for maximum emission flux of materials when predictive modelling was not done.

Table 5. Maximum pollutant emission flux specifications for indoor materials (Tucker 1991)

Material	Maximum Emission Flux
flooring materials or coatings	600 μg TVOC/m^2.h
wall materials or coatings	400 μg TVOC/m^2.h
movable partitions	400 μg TVOC/m^2.h
office furniture	2500 μg TVOC/h/workstation
office machines (central	250 μg TVOC/h/m^3 of space 10 μg ozone/h/m^3 of space
office machines (personal)	2500 μg TVOC/h/workstation 100 μg ozone/h/workstation

These values were estimated from modelling a specific office situation.

One major limitation of this approach is that it ignores the large decrease in emission flux that occurs for wet products. Under most circumstances occupants may not be present in the building during this initial emission "burst". The approach needs to consider the delay in occupancy after application in relation to the speed of emission flux decay, as suggested by Tucker (1991).

Plehn (1990) described the following requirements for low–pollutant paints and lacquers to be awarded the "Environment Label" in Germany:

(a) no constituents which exhibit carcinogenity or mutagenicity,

(b) total VOC content limited to 10% w/w for water–based and 15% w/w for high solids paints (these limits were 0.5 and 5% w/w, respectively, for VOCs with higher "effects potential"),

(c) no heavy metals.

Seifert (1992) recommended a rating system for sheet and board materials based on equilibrium emission flux measurements in environmental chambers. Ratings considered carcinogenic risk, the presence of mutagens, teratogens, toxic and allergenic compounds, irritancy from TVOCs and detection of odour. The scheme was not proposed for use with liquid materials and products that are used intermittently.

Larsen and Abildgaard (1995) proposed evaluation and selection criteria for "paints favourable to indoor air quality". Criteria were based not only on VOC emission characteristics but also application properties and coating physical performance. A specific chamber emission procedure was used as follows:

1. paint was applied (brush or roller) to aluminium plate at a rate to achieve a dry film thickness of 70 ± 5 μm and was then placed (wet) into a chamber;

2. chamber conditions 23 ± 0.5°C, 50 ± 5% RH, 1.0 ± 0.1 air changes per hour, air velocity 0.1–0.3 m/sec, loading 1.0 m^2/m^3;

3. chamber air was sampled at 1–3 hours and 4 weeks after painting; procedures to derive product emission fluxes were not described.

Paints were classified according to VOC emission criteria (of unspecified significance) as follows:

Very best paints:	emission flux at 1–3 hours not to exceed 3500 μg/TVOC m^2.h; after 4 weeks emission flux for individual VOCs and other pollutants less than 7 μg/m^2.h; no emission of "recognised" carcinogens.
Acceptable paints:	emission flux after 4 weeks not to exceed 350 μg TVOC/m^2.h or 75 μg/m^2.h for individual VOCs or 7 μg/m^2.h for recognised carcinogens.

Poorest paints: paints not meeting criteria for acceptable paints.

Paints were also classified according to their odour properties assessed during chamber testing.

Nielsen et al (1993, 1994) described a procedure to assess materials for their potential health effects based on environmental chamber emission flux measurements. These measurements were used to estimate individual VOC concentrations in a "standard" room (for example at 14 and 28 days) in the absence of sink effects and these concentrations were compared to odour thresholds or health-related indoor air exposure standards ("indoor air relevant" concentrations). It was proposed that quantitative risk assessment be used to determine lifetime cancer risks for carcinogens and that levels above 10^{-5} to 10^{-6} were unacceptable. "Indoor air relevant" concentrations were derived from no-observed-effect-levels after imposing safety factors from 100 to 100,000. No criteria were proposed for rating of the products – a concentration/standard ratio below 1 was taken to indicate no odour or health effect potential existed for the particular VOC. An overstepping of this ratio by a factor of 10 was considered acceptable for new or renovated buildings in the first 3–6 months due to the short-term nature of emissions from many new building materials.

Wolkoff and Nielsen (1996, 1996a) extended this approach by proposing a rating parameter which was the time for emissions to decay to the "indoor air relevant" concentration (based on odour or irritation) in a standard room, estimated from environmental chamber (FLEC) emission measurements. Better materials were considered to be those for which all VOC concentrations decayed to below "indoor air relevant" concentrations in the shortest possible time. The procedure was applied to a range of building materials for which the following acceptable decay times (for specific VOCs) were estimated:

waterborne acrylic sealant	7.3 months	(butoxyethoxyethanol)
oil/resin sealant	2.2 months	(dimethyloctanols)
carpet A & carpet B	4 months	(4-phenylcyclohexene)
waterborne acrylic paint – interior	0.4 months	(Texanol®)
– exterior	4 months	(Texanol®).

8. RESEARCH DIRECTIONS

It is clear from research into the drying of film-forming coatings that the physical mechanisms vary markedly as the drying process proceeds and that different mechanisms will be operative for coatings based on soluble resins or on resin latexes. While little information has been found on the drying of stains, substrate porosity may be a factor affecting drying mechanisms of stains.

Evaporation while a coating is still liquid is generally volatility-limited and so VOC emission flux is determined largely by volatilities of component solvents, their quantities and interaction parameters. Precise prediction of evaporation rates in this period is not possible but computer programs are available (eg UNIFAC) for general prediction. Evaporation of VOCs from water-based coatings is further complicated by the effect of relative humidity at application on the relative evaporation of water and organic solvents, and also by partition of solvents between the liquid and latex phases. Volatility-limited drying has been found to occur until solvent contents reduce to approximately 30 to 50% by volume. Thus high-solids coatings may never exhibit volatility-limited drying and conventional coatings will exhibit it only for short periods eg. less than a few hours.

Chamber emission experiments of wet coatings generally place samples in chambers within several minutes of application and follow emission behaviour for several hours to tens of hours. For coatings that do not form dry films (which generally dry fast), volatility-limited evaporation has been clearly observed with first order emission flux decay:

$$EF = EF_o \exp(-kt) \tag{61}$$

Diffusion-limited processes are unlikely for these products unless absorption by porous substrates limits volatility-driven emission. However studies of wood stains on timber have observed only evaporation-limited processes.

For film-forming coatings (ie most paints and lacquers), chamber emission experiments of wet coatings have exhibited anomalies when applying the above source model. This would be expected if the emission mechanism changes soon after application. For example:

(a) Tichenor and Guo (1988) found that EF_o derived for polyurethane lacquer in a 24 hour test did not increase with N/L at high values of N/L, probably due to diffusion limitation of evaporation;

(b) Tichenor et al (1993) found that neither a first order decay model nor a fundamental mass transfer model that was based on a volatility-limited process could be fitted to VOC emission from a polyurethane coating past 15 hours of drying;

(c) Tichenor (1995) found that for the TVOC emissions from a wet PVA latex paint, a first order decay model fit data only up to 7 days, a volatility-limited mass transfer model only up to 30 days and a second order model (indicating diffusion-limited transfer) to 6 months.

The importance of selection of source model lies not only in understanding emission mechanisms but also in the application sink models to chamber data. Late-stage VOC emission that is diffusion-limited could be interpreted as sink-effects if the wrong source model is used and source emission parameters will be incorrectly estimated.

Based on film drying studies, it would seem prudent to apply volatility-limited source models only to the first few hours (or less) of drying of films. However chamber studies have found such models fit emission measurements for 10–20 hours. This discrepancy may be due to the limited air change rate used for chamber experiments (typically 0.5–1.0 h^{-1}) whereas paint drying experiments often used purged chambers (eg. the Shell Thin-Film Evaporometer operates at approximately 40 h^{-1}). Generally, then, chamber measurement of wet coating emission flux should be made only within the first 10 to 20 hours of drying at low ventilation rates and with the assumption that sink effects can be ignored (or by predetermining chamber sink factors for the major VOCs known to be emitted).

As shown by Clausen (1993) and Tichenor (1995) this period might be extended to several days for water-based latex coatings. Some paint drying experiments support this period (eg. Hansen 1974) while many show that water and VOC emission fluxes will drop sharply within hours of application (see Section 3.3.2.1). Further research into wet coating emission behaviour is needed to clarify mechanisms and suitable approaches for interpretation of data.

Air velocity will exert a significant influence on evaporative flux in the volatility-limited region, although this has received little study. Most investigations have used unstirred chambers although guidelines now acknowledge that a forced air velocity in the range of 5–10 cm/sec should be used to simulate indoor environments. While theoretically there is an approximate linear relationship expected between solvent evaporative flux and surface air velocity (Stratta et al 1978, Yoshida 1972, Gunnarson 1991), in practice:

(a) there are many aerodynamic complexities in attaining a parallel, surface-attached and non-turbulent air velocity, even on a flat surface, which precludes true control of air velocity, especially in small chambers,

(b) free convection will cause an air velocity in the 5–10 cm/sec range at the film surface as it dries (Kornum 1982 and Figure 11).

It appears plausible that emission measurements in an unstirred chamber will be more realistic of indoor conditions than those in a chamber with forced convection.

Chamber relative humidity and N/L ratio are expected to be significant factors in the volatility-limited period. Relative humidity will affect the relative evaporation fluxes of water and VOCs (as described in Section 3.3.2). VOC emission flux at 50% RH may bear little resemblance to that at other humidities and so measurement at a range of humidities (eg. 30%, 50%, 70% RH) would provide better assessment. Generally chamber tests use an air change rate (N) and a product loading rate (L) representative of field use. L should not be the total wall/ceiling area divided by internal volume (L ~ 1.2 m^2/m^3) when evaluating VOC emissions from wet coatings in chambers since:

(a) application of paint takes a sizeable proportion of the time the wet coating takes to become semi-dry, and

(b) a more practical situation is considered to be one in which one room of a building is painted and room air circulates throughout the house (for this situation L ~ 0.1 m^2/m^3).

Late-stage VOC emission from paints should be measured at a sufficient time after application for volatile processes to have ceased, eg. after 24 hours for solvent-based coatings and after 10 days for water-based latex coatings (to ensure film coalescence has occurred so that a single source model is appropriate). For this assessment a product loading rate of 1.2 m^2/m^3 would be applicable to simulate painting of the whole interior of a building. Since solvent diffusion in the film is the probable limiting mechanism of mass transfer, surface air velocity should have no effect on emission flux and relative humidity should have very little effect (except a possible plasticising effect by water molecules). Temperature will be a critical parameter as will be specimen preparation procedure. Specimen preparation should closely simulate real preparation conditions to ensure the "semi-dry" stage is reached with a realistic VOC composition (see Section 4.2). Test temperature should be that expected in the building (eg. 23°C). Higher temperatures will significantly influence the diffusion rate, particularly if above the glass transition temperature (Tg) of the polymer (or polymer-solvent mixture). However if chamber experiments are carried out to provide guidance to building bake-out actions, assessment at elevated temperatures will be relevant. As a guide, the Tg of typical latex polymers and coalescing solvents are shown in Table 6 with an estimated Tg for the polymer containing 2% v/v of a coalescent with a Tg of –100°C. Large differences in emission behaviour would be expected for elevated test temperatures depending on the Tg of the polymer-coalescent involved.

Table 6. Glass transition temperatures of latex polymers and coalescing solvents (Hoy 1993)

Polymer or Coalescent	Minimum Filming Temp (°C)	Tg (°C)	Tg′ *(calculated)* °C
styrene-acrylic copolymer A	14	29	25
styrene-acrylic copolymer B	7	26	22
all acrylic polymer A	11	27	23
all acrylic polymer B	<0	–5	–8
all acrylic polymer C	26	37	32
all acrylic polymer D	21	28	24
vinyl-acetate homopolymer A	7	28	24
vinyl-acetate homopolymer B	19	42	38
vinyl-acetate homopolymer C	14	28	24
vinyl-acetate isobutyl acrylate copolymer A	<0	10	6
vinyl-acetate isobutyl acrylate copolymer B	<0	–3	–6
butoxyethoxyethyl acetate	–	–100	–
butoxyethyl acetate	–	–112	–
butoxyethoxypropanol	–	–103	–
ethoxyethoxyethyl acetate	–	–95	–
ethoxyethoxyethanol	–	–103	–
hexylene glycol diacetate	–	–75	–

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APPENDIX A. SYMBOLS USED IN REVIEW REPORT

a	solvent activity
A	area of evaporating surface
ACH	air changes per hour
c_i	vapour concentration of component i
EF	emission flux
C_i	concentration of volatile i in film
d	diffusion constant of vapour boundary layer (volatile diffusivity)
D	diffusivity of solvent in paint film
D_o	diffusion coefficient in paint film at zero solvent concentration
ER	emission rate
f	fractional free volume of polymer/solvent system
F	solvent diffusion flux in a paint film
ΔH_d	apparent activation energy for diffusion
k	source emission decay rate constant
k_d	vapour diffusion rate constant
ℓ	paint film thickness
L	length of evaporating surface in direction of air flow
m'	ration of molar volumes of polymer to solvent
m_t	mass of VOC in indoor air
M	molecular weight
M_t	loss of solvent from coating by weight at time t
MFT	minimum film forming temperature
N_A	surface flux density of A (in g-moles/area/time)
p	vapour pressure of a solvent
p_i	vapour pressure of solvent i molecules in mixture
p_i^o	vapour pressure of pure solvent i
P	external pressure
Q	activation energy of diffusion
R	Arrhenius' constant
R_e	relative evaporation rate
R_e^o	evaporation rate of pure solvent
t	time
T	temperature °K
Tg	glass transition temperature
v	air velocity
V_i	volume fraction of i in solid
w_i	weight fraction of i in vapour
W'	evaporative flux rate (weight/area/time)
x_i	mole fraction of i in liquid
X	Flory–Huggins interaction parameter
γ	activity (escaping) coefficient for departure from Raoult's law
δ	vapour boundary layer thickness
ϕ	volume fraction of solvent in surface layer of film
τ	temperature °C

APPENDIX B. ASTM D3539 Evaporation Rates of Volatile Materials (ASTM 1995, automatic evaporometer data)

Compound	Time to 90% evaporation (sec)	RER
acetone	82	5.7
benzene	133	3.5
isobutyl acetate	305	1.5
n-butyl acetate	470	1.0
sec-butyl acetate	260	1.8
isobutyl alcohol	740	0.64
n-butyl alcohol	1,080	0.44
sec-butyl alcohol	565	0.83
cyclohexanol	9,200	0.05
cyclohexanone	1,570	0.30
diethylene glycol monobutyl ether	150,000	0.01
ethyl ether	27,800	0.02
diethyl ketone	205	2.3
diisobutyl ketone	2,430	0.19
dimethyl formamide	2,280	0.21
ethyl acetate	117	4.0
ethanol	280	1.7
ethylbenzene	562	0.84
ethyl ether	40	11.8
ethylene glycol	–	0.01
ethylene glycol monobutyl ether	6,780	0.07
ethylene glycol monoethyl ether	1,210	0.39
2-ethyl hexanol	25,700	0.02
n-hexane	60	7.8
methyl acetate	93	5.0
methanol	220	2.1
methyl ethyl ketone	121	3.9
methyl isobutyl ketone	280	1.7
methyl n-amyl ketone	1,380	0.34
nitroethane	445	1.1
nitromethane	360	1.3
n-octane	295	1.6
isopropyl acetate	134	3.5
n-propyl acetate	220	2.1
isopropyl alcohol	320	1.5
n-propyl alcohol	530	0.89
propylene glycol	–	0.01
isopropyl ether	57	82
tetrahydrofuran	97	4.8
toluene	235	2.0
water	1,290	0.36
xylene	610	0.77