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STUDIES ON THE REDUCTION OF FORMALDEHYDE EMISSION FROM PARTICLEBOARD BY POLYMERS.

A Thesis
Submitted to the University of Auckland for Examination for the Degree of Doctor of Philosophy in Chemistry

by
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Auckland, NEW ZEALAND,
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* * *

ABSTRACT

Formaldehyde is an important industrial chemical due to its unique properties, coupled with its low cost and the basic availability of the raw materials from which it is produced. It is generated principally by the catalytic oxidation of methanol using a heated stationary catalyst at approximately atmospheric pressure.

Formaldehyde is used in the manufacture of a wide variety of commercial products, the most significant of which in New Zealand, are the urea-formaldehyde resins. Such resins are used in the production of reconstituted wood products such as: particleboard; medium density fibreboard; plywood; laminated and fingerjointed wood products; and in the modification of textiles and papers. Insulating building foams have also been formulated using urea-formaldehyde resins.

Formaldehyde release from products containing urea-formaldehyde adhesives has been well documented in the literature over recent years. It has been shown that in some instances the levels of airborne formaldehyde inside dwellings and commercial premises may exceed various industrial threshold limit values for an eight hour working day. In New Zealand the current industrial permissible time weighted average value for formaldehyde in air is set at a maximum level of 2 ppm (2.4 mg of formaldehyde per metre^3 of air). Natural levels of formaldehyde in air do exist and have been measured as being in the vicinity of 0.12 to 0.39 parts per billion.

In terms of being a health hazard, formaldehyde was found to be a primary irritant of the respiratory airways and a skin sensitizer in some individuals. Some suggestion has been made that formaldehyde can also be carcinogenic. This suggestion should be treated with caution as it derives from preliminary experiments on rats and mice exposed to very high formaldehyde levels.

Over the years a variety of test methods have been applied to the measurement of formaldehyde which is released from formaldehyde-bearing materials. A dynamic testing method, in the form of a wind-tunnel was adopted in this study for measuring the emission rate of formaldehyde directly from the surfaces of urea-formaldehyde bonded particleboard. Emissions were quantified in terms of the weight of formaldehyde emitted in mg from one square metre of panel surface over one hour, under the prevailing climatic conditions.

It was observed that formaldehyde emissions were as great as about 12 mg h^{-1} m^{-2} from panels tested soon after manufacture. After five years of storage of the particleboard panels in ventilated conditions, the formaldehyde emission rates were measured as being between 0.1 and 1.1 mg h^{-1} m^{-2} . It was apparent that formaldehyde emissions from particleboard bonded with a urea-formaldehyde resin with a urea to formaldehyde molar ratio of 1 to 1.5, reached a basal level approximately 12 months from the time of manufacture. The formaldehyde emitted over the initial 12 month period was equated to the formaldehyde which was originally present dissolved in the resin solution and the formaldehyde which was cleaved from the urea-formaldehyde polymer network during high temperature pressing. Formaldehyde lost from the particleboard after the initial 12 month storage phase was probably due to hydrolysis of the resin under ambient conditions. The latter was termed "evaporable" formaldehyde as opposed to "free" formaldehyde which was emitted in the first 12 month period.

The fluctuations in the basal emission rates of formaldehyde from particleboard were attributed to changes in the microclimate associated with the particleboard.

Particleboard panels with a higher density surface layer of wood tended to have higher formaldehyde emission rates in the early period of storage compared with particleboard having a lower density

of wood in the surface layer. Emissions of formaldehyde from the edges of freshly sawn particleboard tended to be as much as 30 to 60 times greater than emissions from the faces of the original panels. After extended storage, emissions from the edges of particleboard tended to approximate the levels of emissions from the faces of particleboard.

It was demonstrated that the presence of an air boundary layer adjacent to the particleboard surface has a significant effect on the formaldehyde emission rate from the panel surface. Below air speeds of 5 cm s^{-1} over the panel surface, it appeared that the rate of diffusion of formaldehyde through the air boundary layer controlled the rate of diffusion of formaldehyde from the particleboard surface into the bulk air. At air velocities in excess of 5 cm s^{-1} the effect of the air boundary layer diminished. It was estimated that within enclosed spaces, such as houses with a relatively low air-turnover rate, the diffusive resistance of air boundary layers to formaldehyde emissions from particleboard surfaces could be significant in lowering the formaldehyde levels inside the house.

The use of paints, paint-coated wallpaper and polymer-coated wallpaper to cover particleboard surfaces tended to reduce the emission rate of formaldehyde to below the detection threshold of the method of measurement (0.01 mg h^{-1} m^{-2}). Some building materials other than urea-formaldehyde bonded particleboard were shown to emit measureable quantities of formaldehyde. These materials were of cellulosic-origin and emitted as much as 0.3 mg of formaldehyde h^{-1} m^{-2}. The latter were known to not contain urea-formaldehyde bonding agents.

The levels of formaldehyde inside a showhome containing urea-formaldehyde bonded particleboard as wall and floor cladding were measured as ranging from 1.2 to 7.2 mg m^{-3}, but these air-borne concentrations of formaldehyde decreased to between 0.7 and 1.3 mg m^{-3}.

after an interval of three months. A mathematical model was derived for the prediction of the maximum expected steady state levels of formaldehyde inside dwellings containing formaldehyde-emitting materials. The model took into account such parameters as: the emission rate of formaldehyde from the emitting surface; the surface area of the exposed emitting material; and the volumetric air flow rate through the dwelling. The model in general tended to indicate higher formaldehyde levels when tested using the parameters derived from measurements taken in the showhome. This model could conceivably find use in the design of buildings in order to minimize the levels of formaldehyde in the indoor environment.

The lack of sufficient information in the literature relating to the mass transfer of formaldehyde through polymers prompted the investigation into the permeability characteristics of polymeric materials to formaldehyde.

The steady state transmission rates of formaldehyde through free polymer films, such as plastic films, free paint and free polyurethane varnish coatings, were measured using a diffusion cell operated at atmospheric pressure. The mass diffusion principle associated with this permeation testing device best paralleled the real-life situation where either polymer films (plastic films) or polymer coatings (paint or varnish coatings) may be in contact with formaldehyde and water vapour, at atmospheric pressure.

As a source of penetrant in these studies a dilute aqueous solution of formaldehyde was used to yield molecular formaldehyde. It was calculated that an aqueous solution containing 69 mg L^{-1} of formaldehyde gave rise to a concentration in air of formaldehyde, above the solution, of 1 mg m^{-3}, at 30°C. A solution with such a concentration of dissolved formaldehyde was chosen arbitrarily for permeation studies. Levels of air-borne formaldehyde inside

enclosed airspaces such as in houses lined with urea-formaldehyde bonded particleboard, with a low air turn-over, could reasonably be expected to be in the region of 0.1 to 100 mg m^{-3}.

The use of carbon-14 formaldehyde was favoured in this research over the use of carbon-12 formaldehyde. This gave rise to the possibility of permeability isotope effects. Based on the information presented in this thesis and on the experimental variability in test results, it appeared that the effects of a permeability isotope effect were negligible in comparison.

The transmission rates of formaldehyde through the following types of polymer films were measured: low density polyethylene; high density polyethylene; high density-low density polyethylene blended polymer; polypropylene; poly(ethylene terephthalate); poly(vinylidene dichloride)-coated poly(ethylene terephthalate); "Paraform", a multi-layered food packaging polymer film based on cellophane; poly(ethylene vinyl acetate), a multi-layered food packaging polymer film; plasticised poly(vinyl chloride); polystyrene; nylon-6; and cellophane. At 30°C transmission rates of formaldehyde ranged from 1.2×10^{-7} µg $cm^{-1}s^{-1}$ for cellophane to 1.2×10^{-12} µg $cm^{-1}s^{-1}$ for poly(ethylene vinyl acetate) polymer films, respectively. There was some indication that the transmission rate of formaldehyde through low density polyethylene decreased with increasing film thickness. It also appeared that an increase in the water contents of nylon-6 and cellophane films lead to an increase in the transmission rate of formaldehyde. With the exception of the poly(ethylene terephthalate)-types of polymer films and the polystyrene film, all other polymer film types exhibited typical Fickian behaviour, in that the permeation of formaldehyde through each polymer film was steady state. The permeation of formaldehyde through

poly (ethylene terephthalate)-type films and polystyrene film appeared to be anomalous in that the mass transfer process did not appear to show Fickian-type behaviour.

The transmission rates of formaldehyde through free alkyd-type paint films, free vinyl-based paint films and through free polyurethane varnish films, were measured at 30°C. The permeation of formaldehyde through free alkyd-type paint films and free polyurethane varnish films typified Fickian behaviour, in that after a short time-lag the steady state permeation of formaldehyde occurred. The transmission rates of formaldehyde through the free alkyd-types of paint film ranged from 1.8×10^{-9} µg $cm^{-1}s^{-1}$ to 3.2×10^{-9} µg $cm^{-1}s^{-1}$ whereas transmission rates of formaldehyde through free polyurethane varnish films ranged from 4.1×10^{-10} µg $cm^{-1}s^{-1}$ to 2.4×10^{-8} µg $cm^{-1}s^{-1}$. It appeared that the "two-pack" or "catalytic-curing" type of polyurethane varnish film had a lower permeability to formaldehyde compared with either "one-pack" ("air-curing") or "one-pack" ("moisture-curing") varieties of polyurethane varnish. By contrast the transmission rates of formaldehyde through the vinyl-based types of paint films tended to range from 3.7×10^{-7} µg $cm^{-1}s^{-1}$ to 6.2×10^{-7} µg $cm^{-1}s^{-1}$.

A study of the temperature dependency of the permeation of formaldehyde through the following polymer film types was made: low density polyethylene; plasticised poly(vinyl chloride); polystyrene; polypropylene; high density polyethylene; cellophane; and nylon-6. The transmission rates of formaldehyde through each of these polymer film types increased with increasing temperature, over the temperature range of 30°C to 50°C, thus typifying Arrhenius behaviour. The energies of activation for the permeation of formaldehyde were calculated as ranging from 16.1 kcal mol^{-1} (67.4 kJ mol^{-1}) for plasticised poly(vinyl chloride) to 33.1 kcal mol^{-1} (139 kJ mol^{-1}) for cellophane, respectively.

These activation energies were in general higher than the energies of activation for the permeation of other penetrants of similar molecular weight, through the same polymer types. The observed energies of activation for the permeation of formaldehyde through polymers were indicative of a strong interaction between formaldehyde and the various polymers.

Desorption studies of formaldehyde from polymer films tested after permeability measurement, indicated that formaldehyde was irreversibly sorbed either onto or into the following polymer film types: low density polyethylene; poly(ethylene vinyl acetate); polypropylene; polystyrene; and plasticised poly(vinyl chloride). Formaldehyde was found to desorb from nylon-6 and cellophane polymer film types, indicating a different type of interaction between formaldehyde and these two polymer film types.

The autoradiography of polymer films and free polymer coatings following permeability testing showed that the pattern of sorbed carbon-14 formaldehyde exhibited by each polymer film type or free polymer coating type, differed according to the type of polymer. Clustering of sorbed carbon-14 formaldehyde in polymer films containing polyethylene polymers may have been indicative of the formation of formaldehyde-formaldehyde polymers or perhaps could have been due to preferred pathways or sites for the diffusion of formaldehyde through the polymer film. The following types of polymer film tended to show a uniform sorption pattern of formaldehyde: nylon-6; cellophane; "Paraform"; free alkyd paint films; free vinyl-based paint films; and free polyurethane varnish films. The uniform appearance of the sorption pattern of carbon-14 formaldehyde may have been indicative of a higher solubility coefficient of permeation for formaldehyde in the latter polymer types. On the other hand, insufficient carbon-14

formaldehyde was sorbed by the poly(ethylene terephthalate)-type and polystyrene films in order to obtain autoradiographs. Both the poly(ethylene terephthalate)-types of films and the polystyrene film had a relatively low permeability to formaldehyde and appeared to also have a low solubilizing effect on formaldehyde.

The data presented in this thesis are discussed in relation to the practical problem that initiated the study. Sufficient detailed information has been collected to enable informed decisions to be taken over the choice of formaldehyde-emitting materials used in the building and the food packaging industries.

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