STYRENE POLYMERS: TECHNOLOGY AND ENVIRONMENTAL ASPECTS

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Contents

The polymers formed from styrene with either isoprene or butadiene are transparent despite their two-phase structure, this difference from a conventional mixture of incompatible polymers being caused by a limitation on the size of the domains. These domain sizes are no greater than about 200 Å, which is much less than the wavelength of visible light, so that there is very little light scattering and the block copolymers are transparent, even though the refractive indices of the two phases are significantly different.

Elastomeric block copolymers are often blended with other thermoplastics to obtain useful compounds. The block copolymer can be either the minor or major constituent. An example of the former would be a blend with polystyrene to give a tough material when incorporated in polypropylene. Even at a level of 10%, the impact strength is improved not only at ambient but also at sub-zero temperatures, without any significant diminution in the rigidity. Examples of the latter would be blends with polyolefins or other flexible ozone resistant thermoplastics (such as ethylene–vinyl acetate copolymers). These blends often have excellent ozone resistance, which is only fully developed in injection moulded or extruded samples.

The block copolymers are not affected by water, alcohol or dilute acids and alkalis but are soluble in ketones, esters and many hydrocarbons. Their solubility is the basis of some of their most important applications in adhesives, caulks and sealants, but they cannot be used where oil or solvent resistance is required.

3.11.3 Unsaturated polyesters

This class of materials falls in the group of thermosetting resins which are cured during the processing stage so that the finished product takes on a three-dimensional structure and is not liable to softening at elevated temperatures in the same way as the thermoplastics. The polyesters are formed by condensing a glycol with both unsaturated and saturated dicarboxylic acids at one and the same time, the unsaturated acid providing the sites within the molecule for the ultimate cross-linking which occurs during the curing stage. The relative amounts of the unsaturated and saturated acids determine the density of the sites at which cross-linking will occur subsequently, and also controls the brittleness of the resin. The polyester resin, with a low degree of polymerisation, is mixed with a reactive diluent, which is normally styrene. Curing of the material during processing requires a catalyst and this is blended into the resin mixture.

A whole range of glycols and acids can be used, but 1,2-propylene glycol is the most important and gives resins which are less crystalline and more compatible with styrene than those formed using ethylene glycol. Maleic anhydride is frequently used as the unsaturated acid with phthalic or isophthalic acids providing the saturated component. Fire retardancy can be improved by using as the saturated acid one containing a relatively high chlorine content such as HET acid which is formed by reacting hexachloropentadiene with maleic anhydride.

The initial condensation on the manufacturing process for polyesters is carried out by heating the acids with the glycol at about 150 to 200°C for several hours; to maintain the colour the reaction is carried out under a blanket of carbon dioxide or nitrogen. Since the condensation leads to the formation of water, xylene is often used to facilitate its removal by azeotropic distillation. The reaction is followed by measurement of the acid number, and it is stopped when this falls to 25–50 (the acid number is the number of milligrams of potassium hydroxide equivalent to the acids present in one gram of the resin). After cooling the polyester, it is blended with styrene (about 30% by weight) and inhibitors added to stabilise the product.

At this stage, the material containing about 30% of unpolymerised monomer must be handled with the same precautions as are recommended for handling monomeric styrene itself with regard to flammability and the physiological effects. Exposure of the resin to the skin may cause dermatitis.

The cross-linking reaction is carried out after the resin has been applied to the reinforcement, usually glass fibre, which is required to give adequate mechanical strength to the finished product. It is achieved by the addition of peroxide catalysts with certain activators and the wide range of suitable products enables the curing to be carried out either at elevated temperatures of about 100°C or at room temperature. Methyl ethyl ketone peroxide is frequently used in conjunction with cobalt naphthenate as activator for cold setting applications.

3.11.4 Miscellaneous polymers

There have been many studies of the polymers of styrene derivatives and some of these are now well established for certain special applications. For example, the polymers of *m*- and *p*-methyl styrene (vinyl toluene) are used in surface coatings.

5

Processing and fabrication with styrene-based polyester resins

5.1 INTRODUCTION

Polyester resins are cross-linked with styrene to produce thermosetting, insoluble and infusible products. The cross-linked resins are usually brittle, and the need to provide reinforcement with glass fibre for almost all purposes has led to the development of a number of distinctive fabrication processes. About 5 or 6% of all styrene produced in the world is used in the production of cross-linkable polyester resins; this amounts to about 650,000 tonnes per annum for the countries from which statistics are available, i.e. those outside the socialist blocs. The control of styrene fumes in the fabrication of products involving polyester resins has been a major problem in the past, although the extent of this problem depends very much on the exact process used and, equally, on the precise conditions of operation. The need to control styrene fumes is now generally recognised, together with the need to minimise airborne dust and glass fibres in the same processes.

A special feature of the glass–polyester laminating industry is that most of the organisations concerned with fabrication are small, and the solutions appropriate for larger concerns are too expensive for the more typical operator. Small companies are especially concerned with the two processes most closely associated with styrene fumes, i.e. hand lay-up and spray-up. As Table 5.1 shows, these are by far the most important polyester processes in Western Europe; the practicability of these processes is a major advantage of unsaturated polyester resins. Further examination of available figures for 1976 shows that there are wide variations between countries. Fifty-five per cent of all glass reinforced plastics material is fabricated by spray-up in Sweden, but only 7% in Germany where the emphasis is on press moulding, and in

TABLE 5.1
RELATIVE IMPORTANCE OF POLYESTER FABRICATION PROCESSES, WESTERN EUROPE (1974)

Process	Polyester used (%)
Hand lay-up	45
Spray-up	25
Press moulding	15
Filament winding	8
Continuous laminating	3
Others	4
Total	100

Source: *Plastics and Rubber Weekly*, 7 May 1976.

the UK hand lay-up predominates. The quantity of press moulding in Norway and Finland is very small, but in the EEC it is a major process. Filament winding is very well established in Switzerland, Austria, Finland and the UK but not in Japan, Norway or Denmark. Continuous laminating is a major process in Italy, Spain and Austria. The US consumption level for glass reinforced plastics in 1976 slightly exceeded the combined totals for the EEC and Japan.

5.2 MAXIMUM ALLOWABLE CONCENTRATIONS

The majority of countries have set maximum allowable concentrations (MACs) for styrene, as for other chemicals, but the values chosen vary considerably from one country to another, and the extent of actual enforcement is unknown. Most regulations refer to a time-weighted average (TWA) which assumes some fluctuations from hour to hour throughout an 8-hour day or 40-hour week. Some also stipulate ceiling levels, above which the concentration of pollutant must not be allowed to rise. The brief periods when the concentration rises above the TWA are known as excursion periods, and must be compensated by corresponding excursions below the average level. Irregular and non-standard working schedules are not easily taken into account. Their implications for threshold limit values (TLVs) have been discussed by

Mason and Dershin, with special reference to solvents known to exert systemic effects as a result of tissue concentration.[1]

The present US Standard, set by the American Conference of Governmental Industrial Hygienists, stipulates an 8-hour TWA of 100 ppm (420 mg/m^3) with a ceiling of 200 ppm and a 5-min period, for any one worker in a 3-hour period, of 600 ppm.

In the UK, West Germany, Switzerland, Finland and Jugoslavia, the TLV is 100 ppm. Sweden has recently reduced its limit to 50 ppm (with a 15 min excursion to 75 ppm) and a further reduction to 40 ppm will apply in 1979. Czechoslovakia, Rumania and East Germany have adopted 47 ppm (200 mg/m^3). Bulgaria and the Soviet Union have limits of 1·2 ppm (5 mg/m^3).

TABLE 5.2
COMPARISON OF HYGIENE STANDARDS IN THE USA AND USSR[2]

Chemical	USA (OSHA 1974) (mg/m^3)	USSR (1972) (mg/m^3)
Acetaldehyde	360	5
Acetone	2400	200
Acrolein	0·25	0·7
Aldrin	0·25	0·01
Aniline	19	0·1
Benzene	30	5
Carbon disulphide	60	10
Chlorine	3	1
Ethyl alcohol	1900	1000
Formaldehyde	3	0·5
α-Methyl styrene	480*	5
Nitrobenzene	5	3
Propargyl alcohol	2	5
Styrene	420	5
Sulphur dioxide	13	10
Toluene	750	50
Toluene-2,4-diisocyanate	0·14*	0·5
Vinyl toluene	480	50

The very low levels for Eastern bloc countries are not peculiar to styrene. For a great many chemicals, US limits are at least ten times as high as those of their Soviet equivalents.[2] This is illustrated in Table 5.2.

The differences indicated in Table 5.2 are even greater than they appear at first sight, because all the Soviet figures, together with those US figures marked with asterisks, are ceiling values; the remainder are TWAs.

According to Zielhuis,[3] the gap between the US and Soviet approaches to toxic limit concentrations has narrowed. The ACGIH now pays more attention to nuisance effects, and to any influence on the nervous system and behaviour, while the USSR Research Coordinating Committee for MACs no longer considers any effect as unallowable in itself, but distinguishes between 'effects' and 'harmful effects'.

In practice, measuring the styrene concentration in a workplace can be quite difficult, because the monomer level fluctuates rapidly with time, and varies from point to point. Equipment for measuring styrene in the atmosphere should be chosen for a specific purpose, e.g.

(1) occasional spot checks,
(2) personal monitoring over a period of hours (in the breathing zone),
(3) continuous monitoring,
(4) warning alarms.

The techniques are discussed in Chapter 6.

Claims that government legislation is not being observed closely in a number of countries are sometimes made. The majority of these reports refer to the polyester–glass laminating industry. In the early 1950s, Rogers and Hooper[4] found concentrations in reinforced plastics workshops ranging from 200 to 700 ppm, although the MAC was then set at 200 ppm. More recently, surveys have reported many cases of the limits being exceeded in Poland,[5] and Olivo *et al.*[6] found the monomer concentrations in Italian polyester plants to be above ACGIH recommended levels.

The TLV does not represent a 'safe limit' for any substance, and the aim should always be to achieve the lowest possible concentrations.

Table 5.3 shows typical styrene concentrations (reported from various private and published sources) in the mid-1970s. It demonstrates the disparity between polyester and other styrene processes; but it must be emphasised that no one set of figures can describe these variable situations in any but the most general fashion.

TABLE 5.3
TYPICAL STYRENE CONCENTRATIONS IN THE BREATHING ZONE, FOR VARIOUS INDUSTRIAL PROCESSES (MID-1970s)

Process	Concentration (ppm)
Styrene polymerisation	2–12
Injection moulding of polystyrene	1–7
Styrene–butadiene rubber production	1–15
Polyester–glass laminating	
Hand lay-up	20–125
Spray-up	10–300
Polyester flooring compositions	10–400

5.3 STYRENE UPTAKE INTO THE BODY

Styrene is normally absorbed into the body by inhalation of the vapour rather than by ingestion or skin absorption. It might be expected that the extent of absorption by inhalation would be a simple function of atmospheric concentration and exposure time, but in fact actual uptake depends on the lung ventilation, i.e. on the rate of working. Uptake is increased by physical work of a strenuous nature, since this increases the breathing rate.[7] The average breathing rate of an adult male in the sitting position is about 14 dm^3 per minute, increasing by 50% with light work, doubling with moderate work, quadrupling with heavy work, and eventually reaching 75 dm^3 per minute with very heavy manual work. Consequently the effects of exposure must be related to job function as well as exposure time and concentration in the workplace.

The following sections are intended to summarise briefly the nature of the fabrication processes and those features of them relevant to styrene emission.

5.4 POLYESTER PROCESSES

5.4.1 Hand lay-up

The traditional method of fabrication involves spreading catalysed resin so as to impregnate glass fibre reinforcement, using a hand-held roller. The operator has to achieve a correct fibre-to-resin ratio and avoid the

production of defects such as dry regions, voids, resin-rich areas, etc. He first mixes the resin with catalyst, ensuring uniform dispersal, and then applies the mixture to a mould. Rolling is necessary to ensure complete impregnation, and must be completed in the short time before gelation (setting) occurs. This is normally about 30 min but can, exceptionally, be much longer. Styrene evaporation is considerable in the early stages of the operation and increases with the intensity of rolling, but falls sharply after rolling ceases and becomes almost insignificant after gelation, unless the laminate becomes hot.

Sometimes the final stage of hardening is carried out in an oven or, for larger articles, a hot room. The removal of semi-finished mouldings from the workshop is beneficial in reducing styrene concentration, whether for hot-curing or not, but a hot room has to be completely separate from the laminating area. Yamasaki[8] describes a Japanese bathtub manufacturing facility which used a hot air room to postcure the products; the styrene concentration in the workshop, normally 50 to 250 ppm, rose to more than 1000 ppm when the drying room door was opened. This situation was improved by installing ventilation.

The completion of cure by treatment at elevated temperature is essential for the removal of residual monomeric styrene, and if the product is to be used for foodstuffs it may require steaming. (Fruits, vegetables, juices, wines, sauces, food additives and drugs are stored or transported in glass reinforced polyester tanks.) Elevated temperature cures are also beneficial in achieving optimum hardness, heat distortion temperature, and rigidity. Whether heat treatments are given or not, fabrication is best carried out in a spacious environment rather than a cramped one.

Hand lay-up is very suitable for the production of limited numbers of large mouldings which require only one smooth surface and where precise tolerances are not important. The method is dependent on the skill of the individual operator, and is in some respects a craft. The most typical products are boats, special car bodies and components, chemical process equipment, caravans and tanks. In recent years some of these markets have been lost to the processes described below, but improvements are still being made; e.g. long-handled rollers, fitted with resin feed metering devices, have the advantage of eliminating hand mixing and removing the operator from the region of highest fume concentration. New applications have been found by combining the rigidity of glass–polyester with the excellent surface finish of thermoformed acrylic shells in composite 'rigidised' structures.

5.4.2 Spray moulding

The application of resin and glass to an open mould by spray gun has the advantage of reducing labour time, although consolidation by hand rolling is not entirely eliminated. There is also a reduction in material costs because the glass reinforcement is in the form of roving, i.e. continuous filament, rather than mat, and there is some saving because of the avoidance of resin waste.

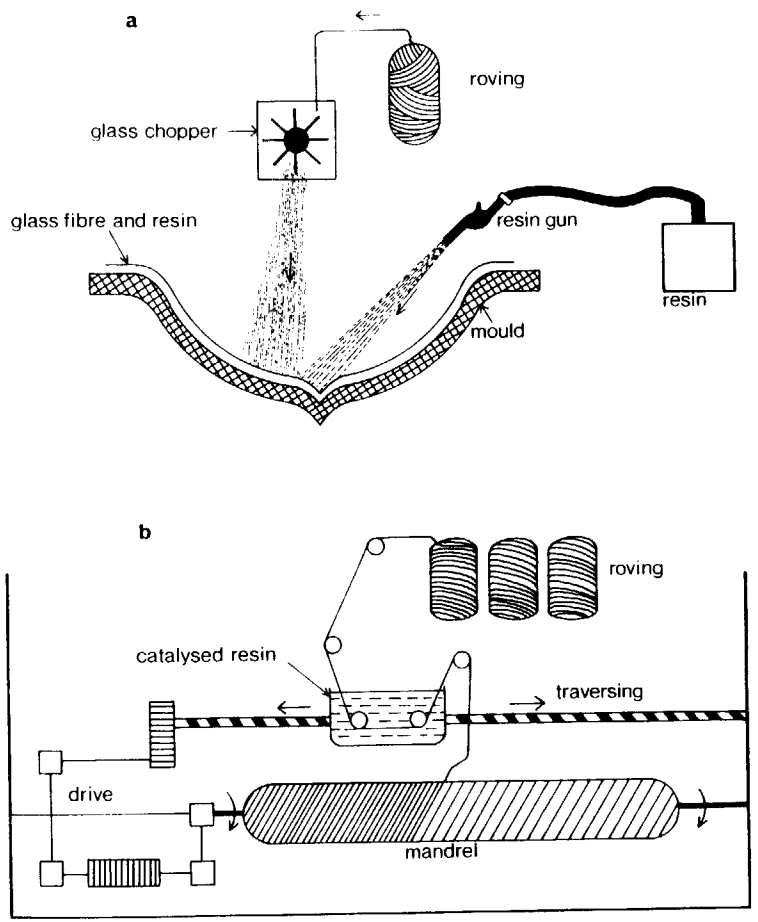

FIG. 5.1. (a) Spray moulding of polyester resin in styrene solution. (b) Filament winding.

Resin is mixed with accelerator and subsequently with either pure catalyst, or catalysed resin. A stream of fibres, formed by passing roving through a rotary chopper, is directed into the resin stream and onto the mould surface (see Fig. 5.1(a)).

The spraying procedure is liable to generate rather high styrene concentrations unless special booths are provided, with good ventilation systems. It is reported[9] that operators of spray equipment are frequently exposed to styrene levels of 500–600 ppm. The concentration of styrene produced in practice is a complex function of workshop lay-out and throughput, resin type, temperature, spray droplet size, etc.

Spray-up is a very widely used fabrication method; in Sweden, for example, nearly 85% of builders of small boats employ high pressure spray equipment, and this accounts for nearly a third of the Swedish reinforced plastics industry. A few spray moulders use tape-controlled robot guns.

5.4.3 Filament winding

For the production of tubes, spheres, cylindrical tanks and pressure vessels, it is the practice to wind roving onto a mandrel. This may either be a stationary mandrel with a fibre feed arm rotating around it, or a rotating mandrel which is wound helically by a traversing feed arm, designed to supply pre-impregnated roving (see Fig. 5.1(b)). Considerable effort has been expended in designing optimum winding angles, feed mechanisms, and mandrels, and also in rendering the process continuous for pipe production. Styrene evaporation occurs, because it is an open-mould process, but the more automated machines do not require personnel to be continually close to the source of styrene as in some other fabrication procedures. It is said that the styrene evaporation can be reduced by using light-cured resins which enable a short gel time to be used with thin section, unpigmented mouldings.[10]

5.4.4 Closed mould methods

Short, chopped glass fibres can be mixed with resin and particulate filler (e.g. calcium carbonate) in an internal mixer, preferably fitted with cooling water and local fume extraction, to give a *dough moulding compound* (DMC) which can be compression moulded in a conventional hot press, in the same way as phenolic and amino moulding compounds. This gives intricate shapes, and achieves fast cycle times, with very little monomer released into the atmosphere. DMC compression moulding is usually semi-automatic but has been fully automated in the latest presses. Injection moulding of DMC has also been developed, increasing the production rate still further by eliminating charge weighing, and reducing cure time by preheating in the barrel. There is also an improvement in quality because of the elimination of handling of the dough, but a disadvantage of injection is the shortening of glass fibres by the action of the screw and by passage through the narrow orifices of nozzle, sprue and gate. Both compression and injection moulding of DMC require large capital outlays and correspondingly large volume production.

Premixes have been developed in a sheet form which is not sticky to the touch, known as sheet moulding compound (SMC). This material owes its practicability to the discovery of chemical thickening agents which convert polyester resins into tack-free doughs by a process of chain extension and agglomeration. This dough is used to impregnate sheet reinforcement. Resin, thickening agent, catalyst, filler and a small quantity of thermoplastic additive are sandwiched between protective polythene sheets and passed through rollers, along with glass fibre mat or chopped rovings. The resulting sheet moulding compound may be hot pressed to give large mouldings of excellent surface finish,

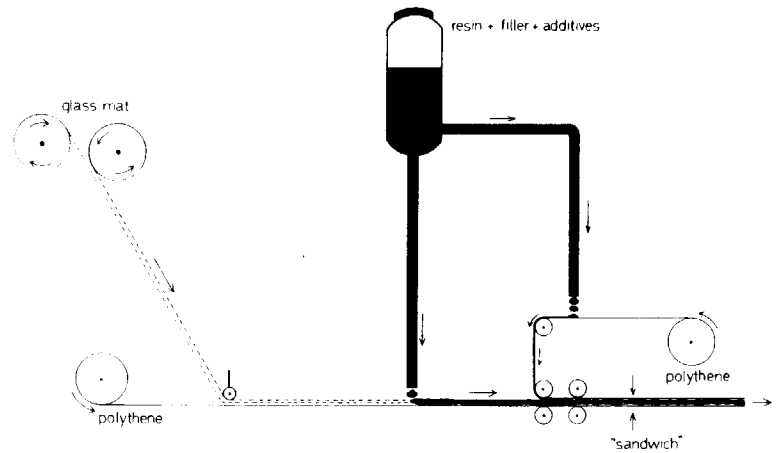

FIG. 5.2. Principle of sheet moulding compound production. The resin–glass–filler composition is sandwiched between polyethylene sheets.

which are used in vehicle bodies, furniture and many other applications (see Fig. 5.2).

The use of any hot press, with high pressures, is impracticable and uneconomic for many large structures. Cold press moulding[11] requires much longer cure times, but otherwise has many attractions. In one version, glass reinforcement is placed in a split mould which is then closed, and resin is injected by a low pressure gun. The moulds may be polyester, epoxy, mild steel, electrodeposited nickel/copper on epoxy, or sprayed zinc/aluminium on epoxy. Filling may be effected without an injection gun, by allowing the resin to flow under gravity into an evacuated mould.

The vacuum injection process has aroused fresh interest because of the recognition of a need for control of styrene monomer concentrations in workshops. The fact that the process uses a closed mould means that styrene concentrations are extremely low.[12] Typical products include building panels, car body components, boat hulls, swimming pools, silos, caravan bodies and roofing.

5.4.5 Other processes

Several other methods have been used for polyester–glass fabrication. Continuous processes have been developed for the production of translucent flat or corrugated roofing, by transferring chopped roving to a moving belt of cellophane web constraining resin. The resin soaks into the glass, and an upper cellophane layer is laid on to form a sandwich, which is then fed through a nip roll into a long oven for curing.

Various bag moulding procedures have been used for many years, including pressure bag, vacuum bag and autoclave processes. The principle is that impregnated reinforcement is laid on a mould and a flexible membrane is then forced against it by positive pressure in a closed vessel or, with modifications, by a vacuum.[13]

Flooring compositions containing no glass fibre, but filled instead with particulate fillers, form a small, though not insignificant part of the total polyester resin market. The spreading of flooring compositions in a confined space can produce high local styrene concentrations. Oltramare *et al.*[14] recorded from 10 to more than 500 ppm, but figures of this sort should not be taken to imply that monomer concentrations are simply functions of the process being carried out. Equally important considerations are the attention given to pollution control, and the size and shape of the working areas in relation to throughput.

5.4.6 Finishing operations

Polyester–glass laminates produced by hand lay-up, spray-up, and certain other processes require trimming and sometimes sanding with power tools. Dust generated by these operations is found to consist of fragments of glass fibre, pigment, resin, and filler. The operator wears a face mask and this offers substantial protection, but at least one country (Sweden) has now prescribed a maximum of 5 mg/m^3 dust per 8-hour working day, and unless further precautions are taken, it is easy to generate 25–100 mg/m^3.

One approach to the problem of dust generation is to fix vacuum attachments to all hand tools and to connect several attachments via a vacuum line system to a central vacuum pump and dust collector. Isaksson recommends a positive displacement pump for vacuum generation and a cyclone separator for heavy dust particles, with a bag house filter for heavy dust.[15]

Drilling laminates, e.g. for the production of printed circuit boards, also produces considerable dust and swarf; this can cause complaints of skin irritation. It will be evident that all machining processes should be scrutinised to keep atmospheric dust to the minimum in view of the numerous additives incorporated in polyester–glass formulations, many of which are of unknown toxicological activity. Styrene fumes are removed before these finishing processes take place.

5.5 STYRENE FUME CONTROL

It will be evident from Section 5.4 that certain polyester processes (chiefly hand lay-up and spray-up) present special problems for the control of styrene, while others do not. So the first option is to develop processes of the closed mould type; these processes predominate in West Germany and account for very large proportions of the Italian and US outputs. Resin injection and vacuum injection processes of various kinds are capable of producing the products presently made by hand lay-up and spray-up processes, but capital costs and the cost of mould construction are higher, and the technology of mould design and of injection needs further development and dissemination.

Given the present reliance on hand lay-up and spray-up methods, examination of the materials involved shows the unique suitability of unsaturated polyesters for their purpose and of styrene as a cross-linking diluent. No other monomer can compete with the low cost, good

compatibility, and good reactivity of styrene. Table 5.4 lists some of the alternatives occasionally used or considered; it is noticeable that most of them would lead to greater problems than styrene.

TABLE 5.4
CROSS-LINKING MONOMERS FOR UNSATURATED POLYESTER RESINS

Monomer	Boiling point (°C)	Characteristics
Styrene	145	Good reactivity, good general purpose products, low cost
Vinyl acetate	72	Too volatile. Inferior weather and water resistance
60/40 *m/p* vinyl toluene	172	Short cure time. Higher resin viscosity. Increased cost
Diallyl phthalate	290	Requires high temperature cure. Higher resin viscosity. Increased cost
Triallyl cyanurate	162 (at 2 mm)	Produces heat-stable products. Requires high temperature cure. Toxicity problems
Methyl methacrylate	101	Volatile; noticeable odour; imparts good weathering; poor cross-linking behaviour
Methyl acrylate	80	Reduced resin viscosity, improved optical qualities. Too volatile
Acrylamide	Solid (melts at 84)	White powder, water-soluble. Requires pressure, not a solvent
Allyl diglycol carbonate	160 (at 2 mm)	Higher resin viscosity and colour. Increased cost
95/5 *p/m* (t-butyl) styrene	219	Poor compatibility with conventional polyesters. Low shrinkage, high reactivity
2-ethyl hexyl acrylate	130 (at 50 mm)	Mild irritant. Flexibilises resin. High cost

The immediate approach has therefore been to reduce styrene emission during conventional polyester fabrication processes, firstly by the installing or upgrading of ventilation, secondly by improved workshop practices, and thirdly by using 'low styrene emission' or 'environmental' resins.

5.6 THE EVAPORATION OF STYRENE DURING HAND LAY-UP

For undisturbed laminates, the evaporation of styrene is in some respects similar to the drying of wet sand, which has been extensively studied. The rate of drying is constant at first (provided that the air above the surface does not become rich in vapour), but eventually slows because of a reduced rate of diffusion through the liquid to the surface.

The transport of a gas through a gas–liquid surface occurs through a double boundary layer by molecular diffusion, and the direction of transport is determined by equilibrium considerations. If an airflow is maintained over the surface, the mass transport per unit time depends on:

(1) the geometrical shape of the surface,
(2) the nature and velocity of the airflow,
(3) the difference between the partial pressure of the vapour and the saturation vapour pressure of the gas at the prevailing temperature.

It is found that the prevailing temperature and the airflow velocity have noticeable effects on the evaporation of styrene from undisturbed laminates. Of the two, temperature is more important and airflow velocity is a minor factor in the range 0·1 to 1·0 m/s. In the absence of any airflow at all, the evaporation rate becomes exceedingly small because of the formation of a still, styrene-rich air layer above the laminate surface. Very high air velocities result in significantly increased evaporation rates.

Rolling disturbs the resin surface and greatly increases evaporation rate. As soon as rolling ceases, the evaporation rate falls sharply again. This is illustrated in Fig. 5.3, which shows what happens when a single layer of chopped strand mat is impregnated by resin in a shallow tray.[16] The resin was poured into the tray at time $t = 0$ and, 5 min later, the reinforcement was added. Rolling took place in one case from the 5 to the 15 min stage. (The figure also shows the effect of added wax; this is discussed in Section 5.7.)

Viscous resins might be thought to lose less styrene, but in practice they require more vigorous rolling, and this results in increased styrene emission. The same effect is found when a grade of glass mat is particularly hard to impregnate for any reason.

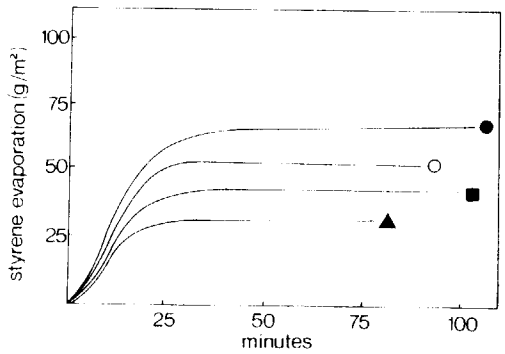

FIG. 5.3. Effect of rolling time on styrene evaporation at 25°C. (Chopped strand mat. Gel time 30–31 min. Air velocity 0·25 m/s.) ○, 10 min rolling; ●, 15 min rolling; ▲, 10 min rolling (with skin-former); ■, 15 min rolling (with skin-former).[16]

Excessive styrene evaporation is disadvantageous not only from the occupational health standpoint but also because it results in laminates which are deficient in styrene or which have variable styrene contents. The idealised network structure of a cross-linked polyester resin has polycondensation chains with number average molecular weight M_n = 1500–2000, and styrene–fumarate polyaddition chains with M_n of the order of 12,000–15,000. The average styrene bridge length is two molecules, with variations from one to six.[17] About 95% of all polyester unsaturation should be utilised (see Fig. 5.4). Loss of styrene results in shorter bridges, unused fumarate sites, or both; the latter produces inferior mechanical properties, and increased water absorption. A study of the effect of styrene evaporation on laminate properties established that water resistance was the most seriously affected characteristic.[18] The nominal styrene content of a resin is typically from 30 to 45% by weight, but this can fall during the fabrication process to 20–33%. This is sufficient to utilise most of the potential cross-link sites of low reactivity and general purpose resins but 20% would be inadequate for highly unsaturated resins. There are some grounds for believing that highly unsaturated polyesters have higher evaporation losses than general purpose resins.

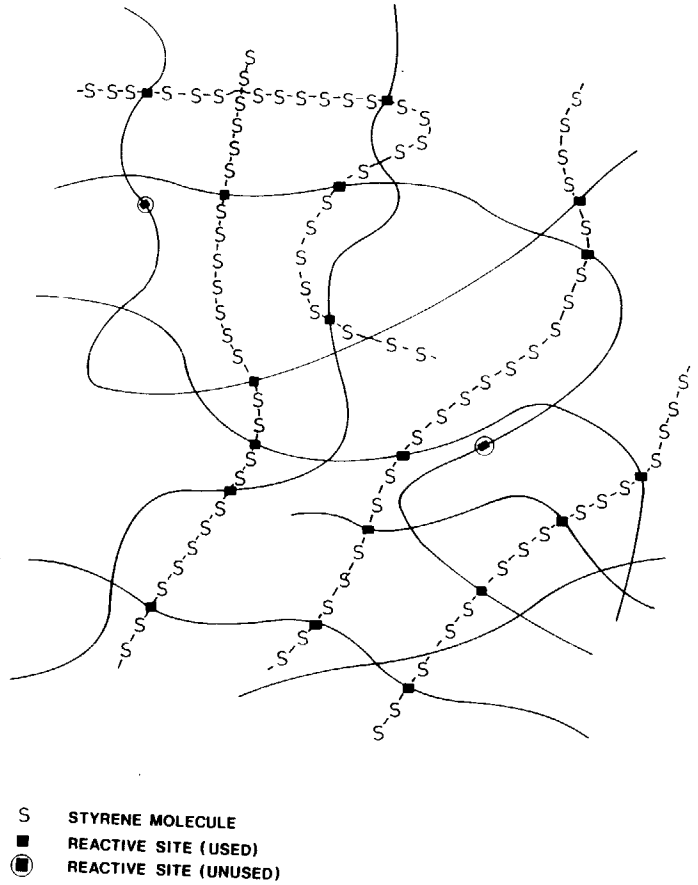

FIG. 5.4. Schematic respresentation of cross-linked polyester resin structure, showing unreacted cross-linking sites.

5.7 VENTILATION

Very small laminating workshops rely on casual ventilation which would be quite inadequate with larger workloads. Considering the example of an unventilated, closed space, the loss of up to 10% of resin weight represents 50–70 g of styrene per square metre of laminate

surface, so it is easy to see that well over 100 m^3 per square metre of laminate would theoretically be necessary to keep the atmospheric concentration below 100 ppm (0·42 g/m^3). But in practice styrene distribution is far from uniform and the concentration in a small 'breathing zone' would soon become too high without ventilation, while elsewhere the concentration would be lower.

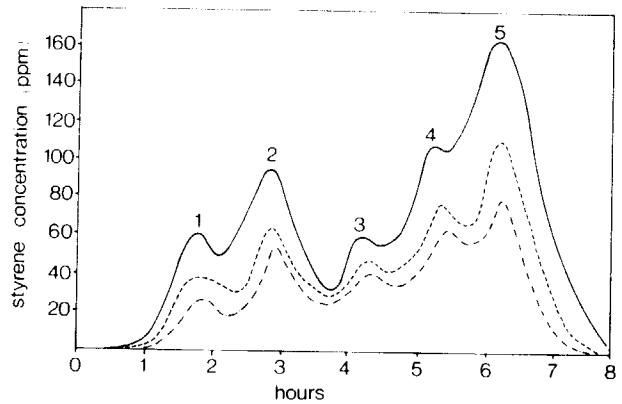

FIG. 5.5. Fluctuating styrene concentrations in a laminating workshop. The dotted lines show the effect of ventilation.

The concentration of styrene in an unventilated workshop reaches a maximum during or just after the rolling stage of the production of a single large moulding. Series production of a number of articles will produce fluctuating concentrations, as shown in Fig. 5.5. The continuous line shows the fluctuations produced by the production of five mouldings in an 8-hour period by operators A, B and C, in close proximity. The production of three laminates in rapid succession is more than the workspace can accommodate. The broken lines show qualitatively the effects of moderate and improved ventilation in lowering peak concentrations. (Concentrations are averages, based on measurements at the three locations.) One improvement is to remove laminates as soon as possible from the laminating shop. A hot air drying room should be positioned remote from the laminating area and should be vented.

The simple replacement of styrene-rich air by ceiling-mounted extraction fans is expensive, particularly because of the need to heat

incoming air in winter. It is also an inefficient way to remove vapours from the breathing zone.

Localised ventilation has the advantage of being more effective and, in the long run, more economical, and practical methods have been investigated by the Swedish Plastics Federation. The conclusions are given by permission of Isaksson[19] (who directed this project) and of Scandinavian Glasfiber AB.

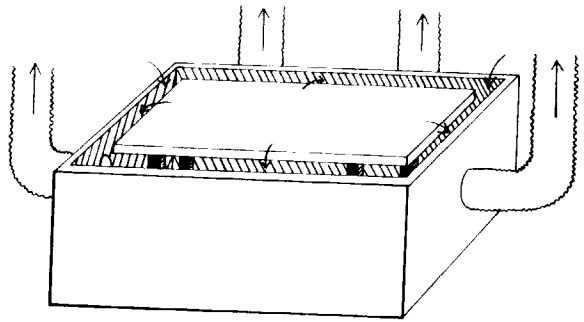

FIG. 5.6. Laminating table with vacuum cowl and four low-level ducts (after Isaksson[19]).

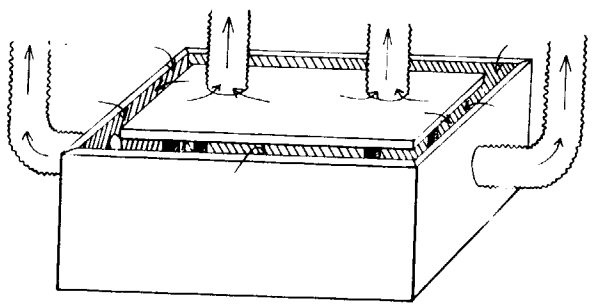

FIG. 5.7. Laminating table with vacuum cowl and two low-level ducts, with two more nearer the laminate surface (after Isaksson[19]).

Figures 5.6 and 5.7 represent in principle the methods Isaksson tried. He partitioned off a 12 m^2, draught-free area with polythene sheeting, and measured styrene concentrations during lay-up on a workbench fitted with four extractors at floor level around the bench. The capacity

of the four hoses totalled 6000 m^3/h, and the maximum styrene concentration found during the lay-up of a product on the bench was 75 ppm. By constructing a vacuum cowl around the bench, this was reduced to 20 ppm (Fig. 5.6). Moving two of the hoses to points 200 mm above the laminate surface reduced the concentration to 3.8 ppm, although it may incidentally have increased actual loss from the laminate surface (Fig. 5.7). The improved results from placing ducting adjacent to the laminate led to a further test in which the cowl and its lower hoses were removed, and a single benchtop hose at 2000 m^3/h was left. This gave a peak reading of 17 ppm. It can be seen that very considerable extraction rates were used in relation to the total working area.

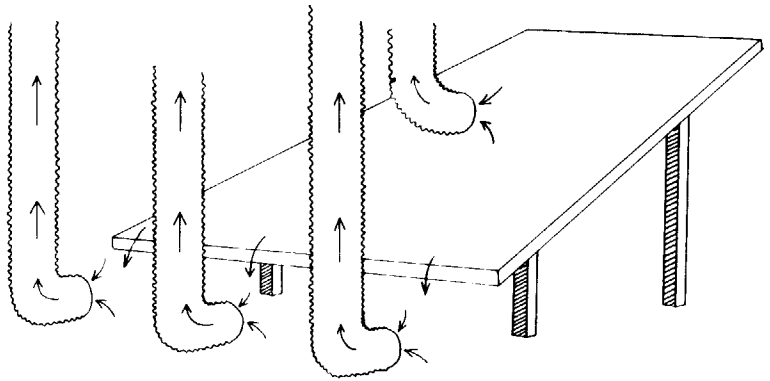

FIG. 5.8. Sloping laminating table (after Isaksson[19]).

Further investigations with arrangements similar to, but not identical with, those illustrated, some with sloping tables (Fig. 5.8), led to the conclusion that several extractors rather than one should be mounted close to the laminate surface. The extractors have to be fitted with protective filters to prevent them from taking up pieces of glass fibre or other small objects, and should be sited to minimise inconvenience through obstruction of work. The air removed should be replaced with diffused air supplies fed through wall- or ceiling-mounted grids, as this avoids the turbulence produced by localised inlets, and can reduce concentrations drastically compared with those in undiffused air.

Some shapes of laminate pose special ventilation problems because

they require the operator to work inside hollow shapes, e.g. large boat hulls, storage tanks, etc. Evans[20] discusses this question and recommends extraction from within the moulding via one of the openings, with the other openings temporarily sealed. Work should be progressed from the extraction point towards the air inlet, rather than the reverse. The working temperature is lowered substantially because of rapid air changing.

Ventilation is also required for spray-up. Spraying can generate styrene concentrations as great as or greater than those produced by hand lay-up; the concentration in an unventilated space of given volume depends on spray pressure, droplet size, delivery rate and resin type. Low pressure spraying is said to produce higher concentrations than high pressure techniques. Nozzle design and the catalyst mixing method are also important.

Again, a single powerful wall-mounted extractor behind the mould can be effective but expensive. Mouldings have to be removed from the extraction zone after spraying to make room for others, and can still evolve considerable monomer.

Alternatively, a larger area can be curtained off (an important step in itself) and ventilated by diffused air from the whole of one wall, while the operator sprays towards the opposite wall where an extractor system is fitted.

The extraction of styrene-rich air produces significant styrene concentrations in the immediate vicinity of a factory if the air is vented without further treatment. A disposable filter pad will absorb the dust, glass fibres and resin droplets inevitably picked up by highly localised ducting; the filtered air still contains styrene, but this can be absorbed by passing through an activated charcoal scrubber. (The function of the pad is partly to protect the scrubber.) Pads have a long usable life (typically several months) between replacements, but charcoal and other absorbing materials become saturated more quickly. The useful lifetime of charcoal absorbing plugs is very dependent on the styrene concentration in the extraction stream.

Regulations for styrene concentrations in factory exhaust stacks and at 'ground' level (i.e. 1 m above ground) vary. One country has proposed exhaust concentrations[21] of 150 mg/m^3 with ground level concentrations of 0·2 mg/m^3 (0·048 ppm). The collection of emission products is not difficult in principle but collecting devices increase the power requirements for maintaining extraction flow rates.

5.8 ENVIRONMENTAL RESINS

Resins differ in their tendency to lose styrene. Important factors include:

(1) original styrene content,
(2) viscosity (related to styrene content and molecular size),
(3) wet-out time (related to viscosity),
(4) the ratio of saturated to unsaturated acid components,
(5) the presence of pigments or fillers,
(6) the presence of skin formers,
(7) gel time.

In order to achieve a really low original styrene content without an unacceptably high viscosity and long wet-out time, the resin must have a low molecular weight, and high acid number. This is unsatisfactory because low molecular weights result in poor mechanical properties and high water absorption. It is therefore uncommon to produce resins with less than 28% (w/w) styrene, but efforts are made to avoid the necessity for more than 40%.

Resins specially designed to give low styrene concentrations during lay-up often incorporate a skin-former. This migrates to the surface after the catalyst is added but before gelation, and so forms a barrier preventing the evaporation of styrene. Skin-formers can also be introduced by the incorporation of air-drying groups into the resin.

Migratory film formers are much more effective in thixotropic resins than non-thixotropic ones, and also much more effective with volatile cross-linking monomers (such as styrene) than less volatile ones.[22] They consist of paraffin waxes, stearates, certain polymeric compositions, or any suitable substance possessing marginal compatibility with the resin to enable it to be dissolved, yet which becomes insoluble as a result of the resin being used. It is not always cross-linking which causes the skin-former to become insoluble; wax migrates to the surface of uncatalysed resin almost as quickly as to the surface of a normal cross-linking resin. Styrene evaporation is probably the main factor disturbing the solubility of the skin-former. The evaporation acts in two ways: by removing solvent, and hence increasing solute concentration; and by cooling the surface. The effect of wax concentration on styrene loss from an undisturbed laminate in the absence of gelation is shown in Fig. 5.9.

Very careful matching of additive with resin is necessary. It is not

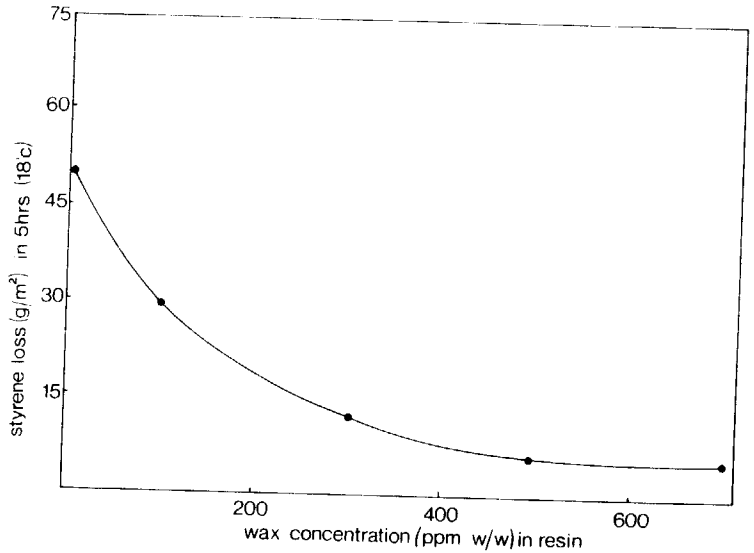

FIG. 5.9. Effect of wax concentration on styrene evaporation from an undisturbed laminate in the absence of gelation (18°C).

sufficient to select the 'right' additive; it must have precisely the correct compatibility with the particular resin in which it is used. Otherwise, normal storage with temperature fluctuations results in premature film formation, and some of the resin then contains very large quantities of additive while the latter contains none. This is believed to contribute to adhesion failure in a few instances. Delamination by impact is said to occur more readily in wax-containing systems.[22]

Other related objections have been raised to the use of 'environmental' resins for styrene control. One is that a skin-former acts as a mould release, reducing interlaminar adhesion during delayed lay-ups, i.e. procedures in which some of the reinforcement is impregnated a long period after the first few layers.

These objections have been investigated for one particular resin–wax system, having good mutual compatibility, by Haigh, Pritchard and Swampillai.[23] Their measurements were made using both model experiments (single-filament specimens of a kind designed by Outwater and Murphy[24]) and ordinary laminates for conventional lap shear and short-beam shear strength tests (see Fig. 5.10), using woven roving reinforcement. There was no significant effect in the range 0 to 1000

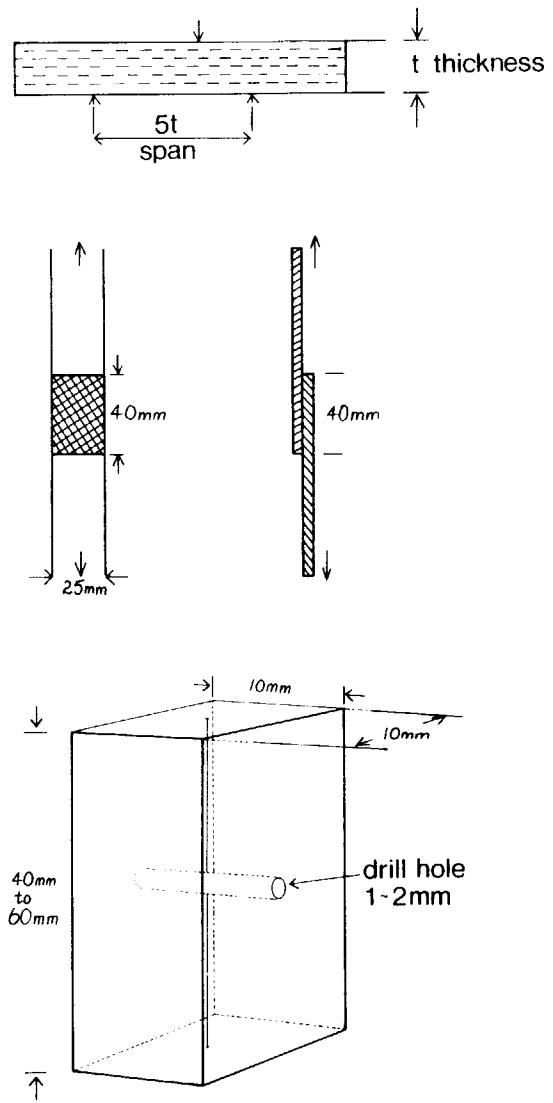

FIG. 5.10. Specimens for determining the effect of skin-formers on adhesion in laminates. *Top:* apparent inter-laminar shear strength. *Middle:* lap shear. *Bottom:* compression block containing single fibre (not shown) embedded in the centre of the block, parallel to the longest dimension.[24]

TABLE 5.5
MECHANICAL PROPERTIES OF ISOPHTHALIC POLYESTER LAMINATES AS A FUNCTION OF PARAFFIN WAX CONCENTRATION

Wax concentration (ppm, w/w)	Short-beam shear strength (MN/m^2)		Lap shear strength (MN/m^2)
	Series A	Series B	
0	17·3	21·8	4·9
100	17·4	—	—
500	—	22·6	—
1000	17·9	23·8	4·7

ppm paraffin wax (see Table 5.5) but this does not mean that other wax–resin combinations necessarily produce the same effect.

Series A specimens were 8-ply laminates produced by adding four plies to the first four after a delay of 20 days. Series B specimens were 9-ply laminates (3 layers impregnated at a time, with 24 h delay between each group of three). Some of the series B laminates were subsequently aged in various environments, but in no case did the presence of a styrene-suppressing additive affect the ageing characteristics (except possibly, and only slightly, prolonged immersion in petrol). The results of the model experiments with single glass filaments showed a greater dependence on various artefacts, e.g. humidity, than on wax concentration.

Another, rather more obvious point is that skin-formers can act only between the end of the impregnation stage and gelation. This is quite often a short period, and is not in any case the time when the operator is most at risk. But the cumulative effect of measures which, taken singly, seem to amount to little, has led many fabricators to prefer resins of this kind. The development of a satisfactory resin is a long way off and, at present, ventilation offers the most substantial benefits in styrene control.

5.9 OTHER PREVENTIVE MEASURES

5.9.1 Temperature control

In practice, laminating is carried out between 10°C and 30°C, depending on climate and air conditioning. The importance of temperature in increasing the partial vapour pressure of styrene, and hence its

evaporation rate, has been implied in Section 5.5 and verified by experimental observation. Typical changes in evaporation rate between 15°C and 25°C are indicated in Table 5.6. Increased evaporation at high temperatures is accompanied by reduced working efficiency, and shortened gel times for pre-accelerated resins. The flash point for styrene is about 31°C (88°F). At the lower limit, problems are found in curing resins below 10°C because of slow and incomplete reaction.

TABLE 5.6
EFFECT OF TEMPERATURE ON EVAPORATION RATE[23]
(AIR VELOCITY 0·25 M/S)

Original styrene content of resin (%, w/w)	Workshop temperature (°C)	Styrene loss (g/m²)	
		During 10 min rolling	During first 30 min (including 10 min rolling)
40	15	36	64
40	25	67	96
30	15	35	49
30	25	50	67

5.9.2 Protective clothing

The operator, both in hand lay-up and in spray moulding processes, has a double function to carry out. He has to produce the moulding and also to inspect it for defects before it is too late to remedy them. As a result he works close to the laminate surface, and is exposed to high local concentrations. Protective anti-styrene, anti-dust suits are available for laminating shops, consisting of helmet, visor, jacket, belt, and, if necessary, clean air supply line with regulator valve and air-filter. A major disadvantage of all protective clothing is the hindrance to movement, and widespread adoption of suits is difficult to enforce.

Respirators have been widely used for protection against dust, but again there is a reluctance to use them for long periods because of poor fit, discomfort, restriction of movement or speech, and their tendency to collect dust and dirt. They need frequent cleaning; those with visors soon suffer a loss of transparency because of dust scratches. Full face masks are essential for eye protection at styrene concentrations above 400 ppm, e.g. if work is carried out in a closed space.

Respirators using carbon cartridges should have their cartridges

replaced frequently. The lifetime of cartridges depends on the user's work-rate, but can be estimated approximately from the discussions of Nelson and Correia;[25] the conclusions can be applied to extraction unit filters.

Nelson and Correia assume that the adsorption of styrene by activated carbon in the cartridge depends on styrene concentration, air temperature, etc., in accordance with the adsorption isotherm:

$$w_s = \rho W_0 \exp\left\{\frac{-BT^2}{\beta^2}\left[\log\frac{p_s}{p}\right]^2\right\}$$

where w_s = the equilibrium static adsorptive capacity per unit weight of carbon (g/g); ρ = density of styrene (g/cm³); W_0 = total volume of adsorption space (cm³/g); B = microporosity constant for the carbon; T = temperature (K); p_s = saturation vapour pressure of styrene at T°; p = equilibrium partial pressure of styrene; β = affinity coefficient of styrene vapour for the activated carbon; and, from this equation, they deduce a relationship between cartridge service life, t_b, and average styrene concentration, c. They conclude that, for two different concentrations,

$$\frac{t_b}{t_b'} = \left(\frac{c'}{c}\right)^4$$

so that if the concentration is diminished 10-fold, the service life is increased 4- or 5-fold.

Different devices are needed where very high styrene concentrations are involved, such as in cleaning styrene tanks. Full face masks are necessary for eye protection above 400 ppm, and hose masks are required wherever oxygen deficiency is suspected. These can be used up to 8 m from a fresh air supply; they are not required for glass fibre–polyester work.

Hand protection is of two kinds: gloves and barrier creams. Polythene or rubber gloves (polychloroprene, or nitrile rubber) can be worn for protection against styrene, resins and dust. Polythene has the advantage of not containing additives which are themselves known to be skin sensitisers. Both types are as effective in preventing the evaporation of sweat as in keeping chemicals out. Sidi *et al.*[26] consider that sweat is itself an irritant for skins already affected by eczema.

Lefaux[27] makes a similar point that barrier creams can be of great use in protecting against primary irritants, but fail to protect those who are already sensitised. They can sometimes actually facilitate penetration of the skin.

Hand washing should be carried out carefully without abrasive action, and styrene-based polyester resins should not be removed with organic solvents such as acetone.

The action of styrene on the skin is discussed in Chapter 7.

5.9.3 First aid for styrene exposure

Clothes contaminated with styrene should be removed and the skin, if splashed, washed with mild soap and water. Eye splashes should be dealt with by prolonged (15 min) eye irrigation with clean water, with eyelids raised. These operations should preferably be performed away from the contaminated atmosphere, in fresh air. High concentrations of styrene vapour can cause drowsiness, and persons affected by this may be unresponsive. Styrene is capable of anaesthetic action in the extreme case.

It is unlikely that liquid styrene will be swallowed, although an inexperienced person might ingest a very small quantity. It is found to cause irritation of the mouth, oesophagus and stomach.

A few individuals are particularly sensitive, not only to styrene, but to a whole range of organic chemicals. These persons, together with those suffering from liver, kidney, nervous system, blood or haemopoietic organ disorders, and women with ovulation or menstrual cycle disorders,[28] should preferably never be employed in industries which require exposure to high levels of hydrocarbon. Medical screening of employees prior to appointment, followed by medical examination at periodic intervals, is a contribution to the prevention of health problems.

5.10 ECONOMIC ASPECTS

The reduction of the styrene TLV to 50 ppm in Sweden has caused problems for the industry in that country, but the long-term competitiveness of the majority of fabricators may have been strengthened and their efficiency improved. The costs incurred include installation of ventilation, rearrangment of working accommodation, purchase of styrene monitoring equipment, maintenance of extraction systems, and extra electric power consumption both for circulation and heating. This is in addition to similar expenditure for dust control.

Compensations are also evident: improved working conditions imply reduced labour turnover, and better retention of skill and experience, in an industry which relies more on these qualities than is sometimes

believed. Medical evidence suggests that high styrene concentrations are linked with operator lethargy, aggravation of minor respiratory and other complaints, and even accident-proneness. It is difficult to quantify the benefits of alleviating such a problem, but the results must be reflected commercially.

The total quantity of styrene 'lost' by evaporation per year throughout the world can be estimated from the known losses in typical hand lay-up operations, and may be as high as 80,000 tonnes (worth 35 million US dollars at 1978 prices). Installation of ventilation does not reduce this quantity; on the contrary, it could increase it.

Environmental resins reduce the wastage by only a small fraction, because the quantity of styrene in a resin is determined by viscosity and other considerations as well as cross-linking requirements, and the losses occur during rolling. A substantial saving would be difficult to achieve by any presently available method. The ideal would be to collect and reuse evaporated styrene and the feasibility of doing this has been examined by Maguire and Currieo.[29] They absorbed the styrene in a column down which dibutyl phthalate was flowing, and found it possible to remove 90% of the styrene from the air stream in this way. The styrene collected was distilled from the dibutyl phthalate which in turn was to be reused. The installed costs and operating costs of the process were high, and at present recovery is not economic for most polyester operations.

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