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Styrol emission reduction during the processing of unsaturated polyester

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Abstract: Plastic products are widely used in our everyday life. During the the production and use of different plastic products, adverse health effects are often arising. Styrol plays a decisive role in the good mechanical aspects and heat resistancy of ready made form pieces of unsaturated polyester resins. The styrol contents of the unsaturated polyesters are quite high, the combination(mix) of styrol and polyester gives the typical characteristic features of these sytems while a number of health and fire protection problems come to the surface during their application.Risks can be significantly reduced by the modification of the manufacturing process, application of preventive actions, properly informing employees, and using new organisational solutions.

1 Introduction

Nowadays plastic products have been become our daily devices, articles for personal use; these are irreplaceable in modern offices, homes, in components of vehicles.

Several scandals, films have drawn public attention to missing health protection of plastic production workers and to the problem of poisonous waste management.

More chemical companies buried steel barrels filled with hazardous waste: the barrels rusted and the poisonous toxic materials leaked into the ground, and supposedly as a consequence the cancerous morbidity has risen in the affected area.

Industrial safety organizations have been examining for decades the health damage characteristics of emission occurs in the course of distribution, assembly, utilization of certain plastic products.

Unsaturated polyester resins - the components of fibreglass polyester – were started to be produced in industrial size more than 40 years ago in the developed countries of the world.

From products made of fibreglass polyester (e.g. children's toys, ships, drain elements, tanks, automotive components, sanitary goods) are produced some 2 million tons per year around the world.

During automatic and manual workflows, in the complete technology process (laminating, gelation, hardening) significant volume of styrene monomer gets into the airspace of the plant.

Styrene is an indispensable component of unsaturated polyester resins, play a determining role in the conformation of adequate mechanical and heat resistance characteristics of the finished moulded pieces.

Styrene content of unsaturated polyesters is usually between 30-50% so the combination of styrene and polyester results the typical features of these systems; on the other hand several health protection, work safety, fire prevention problems occur during the application.

My essay analyses the possible methods of styrene reduction in the conversion of fibreglass cored polyester, a partial area and its components; focuses first of all to the diminution with organizational factors.

2 Dangers in application of unsaturated polyesters

The domestic and international industrial and health safety organizations analyse the effects of solvents occurring during the manufacture and application of substances, products in the moment of birth of certain materials and technologies.

The unsaturated polyester-related inspections search the answer that the evolving substance from solvents how endangers user and its environment from the aspect of work, fire and health safety.

My research examines the health damage effects of styrene, which is a component of unsaturated polyester used during the manufacture of fiberglass polyester products, and sets the aim to reduce the emission with organizational methods.

Several literary references are available in connection with the health damage effects of styrene monomer. These scientific publications construe the clinical methods and results of human and animal experiments. In 1976 – based on the experiment sequence made by Stewart et al - an international committee defined first the concentration maximums which can be allowed in plant airspace at the technologies potentially conjunct with styrene exposition.

In most of the European countries the styrene content of working space air is regulated, which is indicated with TLV (Threshold Limit Values) for the maximum permissible styrene concentration (ppm – part per million – mg/kg) in air; these are average values relevant for 8 hours working time.

According to the operative EU-classification styrene is not carcinogenic. The German research institute which deals with determining MAK**1** values classified styrene as 5. category carcinogenic substance, means that although styrene is carcinogenic and gene-toxic substance but the effect is so low, that if the MAK values are observed there is no carcinogenic matter related to human organism.

According to the earlier valid 21461/1-88 Hungarian standard styrene is K-marked, i.e. qualified as carcinogenic substance.

From carcinogenic aspect the Hungarian regulation adapted the international classification, but considering emission it is more rigorous; therefore particularly important to take all means and possibility into consideration in order to reduce emission.

Workers get in direct touch with styrene primarily at the high proportion existing manufacture-style technologies (e.g. shipbuilding).

Polyester resin is allowed to contain styrene in 25-50%.

Closed flash-point °C	Explosive limit				Relative vapour density	MAK-value, mg/m³	TLV [ppm]
	Lower		Upper				
	g/m³	Tf%	g/m³	Tf%			
31	47,5	1,1	345	8	3,59	50	12

Chart 1
Main features of styrene
Source: ICSSC: 0073 data sheet - own edition

Styrene absorbs on skin surface, makes it dry and rough to the feel, a long duration contact can cause dermatitis or allergy for highly sensitive individuals.

Brooks et al. examined the efficiency of protecting equipment (protective gloves, clothes, gasmask) to avoid styrene harm, and it was detected, that with the right application workers' health care protection is guaranteed.

Typical problem of polyester converting plants is odour load. The odour threshold value of styrene is very low, 0,005 ppm, that means that the presence of 0,01 mg of it is already perceptible. Permanent odour effect can result headache, nausea, lack of appetite for highly sensitive individuals.

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[1] **M**aximale **A**rbeitsplatz-**K**onzentration, highest allowed workplace concentration

Vapour of styrene irritates the eyes, respiratory tract, and skin surface also in relatively low concentration, in case of sensitive individuals skin contact can cause eczema. During more years work can have a damaging effect on central nervous system and also on liver.

At concentration of 300-400 mg/m³ the presence of styrene is highly perceptible, causes burning feeling in eyes and respiratory tract, according to individual sensitiveness can cause headache, vertigo, nausea, and somnolence. At extremely high concentration (above 5 g/m³) styrene is highly irritates the mucous membranes, eyes, and burns skin during a short time.

Further increase of concentration causes spasms, mainly stomach spasm then loss of consciousness.

3 Materials and methods, aims

To analyse emission reduction possibilities I chose a plant in the South Plain region of a company producing mainly with manual, manufacture-style technology.

Before starting examination maintenance, filter change was not implemented; the plant conditions were not altered.

Laminating working area is 18 m long and 12 m wide with 3,5m headroom, operating with an upper-arranged heatblast, 15 m3/h power lower-exhaustion accomplishing air technology.

The company makes the polyester conversion with open-mould processing through manual laminating; the largest emission is realized even under these conditions.

Manual laminating means that a well-proportioned mix of polyester resins, fibreglass and a certain initiator-activator is applied with a teddy roller or brushing onto the finished negative moulded pieces in the right thickness.

Production technologies	**Styrene loss [%]**
Gel coat spraying	**10-14**
Spraying, not with LSE resin	**7-10**
Gel coat lubrication	**6-8**
Manual laminating, not with LSE resin	**4-6**
Spraying with LSE resin	**4-6**
Topcoat spraying	**4-5**
Topcoat lubrication	**3-4**
Manual laminating with LSE resin	**3-4**
Laminating (continuous)	**1-2**
Closed technologies	**<1**

Chart 2
Styrene emission in certain production technologies
Source: NOVIA Kft. Dangers of styrene emission

During examination I did not use LSE (Low Styrene Emission) or LSC (Low Styrene Content) resins, I did not change the additives, ventilation, I only raised the temperature in a given period all in all.

Possible methods for styrene emission reduction

- Material selection
    - material selection (using LSE and LSC resins)
    - usage of additives
    - volume and replacement of (co) monomer

- Technology selection
    - Open
    - Close
    - Choosing right temperature

- Ventilation
    - local exhaustion
    - general ventilation of the plant

- Organizational, human factors
    - keeping distance from styrene emission
    - blocking the effects of emission source
    - emission source separation
    - personal separation
    - individual, personal protection

The aim of the for 5 days, 3-3 hours lasting examination was to have a general overview that some human and organizational factors and temperature alteration how affects the styrene content in airspace.

Further aim of the examination is to provide a basis for direction determination and planning of the research.

During the examination 4 persons were working in protective mask. 10 pieces of 75*120*20 cm sized tanks were finished with 4mm thickness, using 240 kg resins.
During the examination no rain fell, the average external temperature was between 17-19°C, strong sunshine did not influence the work in the conversion room.

Fresh air change and the temperature of the room were provided with warm air blasting by gas-fired boiler.

For measuring styrene concentration I used a simple glass tube, which gets discoloured under the effect of styrene. The value of styrene concentration is given by the degree of discolouration. This tool is suitable for immediate measurement of air styrene concentration, but cannot replace the methods which are reproducible and give exact measurement results.

4 Evaluating the results

Wilful failure		Degree of discolouration
Raising temperature from 18°C to 30°C	1st day	significant
Removing the cover from storage elements	2nd day	medium
Spraying in laminating room	3rd day	significant
Raising thickness from 3mm to 5 mm	4th day	medium
Removing work piece	4th day	medium
Storing finished work pieces in laminating room	4th day	medium
Reduction of filter area	5th day	medium
Opening doors and windows	5th day	medium

Chart 3
Connection between wilful work failures and increasing styrene concentration
Source: own measurement, own edition

The increasing styrene monomer in airspace can be originated from several human and organizational factors (failures), which can contribute to excess limit.

Results of 4-5 days show cumulated effects, as the indicated failures are committed usually at the same time.

Typical organizational failures

a. laminating procedure is physically not separated from other plant departments

b. working with liquid resins were not restricted to a separated area and the work sections are shaped that the work process emitting more styrene is placed to the fresh air-input side and the work process emitting less styrene is on the other side, next to the aspiration throat of the ventilation system, in which case the upper air breeze blows the released styrene through the worker

c. workflows accompanied by high emission - e.g. gel spraying or laminating extra-large surfaces - are done at the beginning of the working day so parallel more styrene emitting processes are implemented

d. complete cross-linkage of moulded pieces not implemented in a separated room

e. worker change-over in a suitable time is not organized, so the daily average styrene load can increase

f. the tool is allocated on the largest distance from the exhaustion, the worker does his job with moving around the tool so the fresh air breathing is not secured

g. filters in exhaustion channels can be stuffed by fibreglass, so the air resistance grows, the ventilation gets worse

h. doors and windows are opened during workflows, so air turbulence evolves one side and released styrene gets out without control from the workspace on the other side

i. first line is fixed with strong catalysing, the winding for exhausting and compacting is out of use, therefore the styrene evaporation happens earlier than the gelation

j. gasmask is not used neither during the works done inside the larger laminated objects, equipment nor during the spraying

k. the upper layer of the moulded pieces is not covered during the process of hardening

l. not every source is covered from which styrene can release (open barrel, bucket)

m. volume of materials with styrene content is not minimized in workspace

n. during spraying over-spraying happens in more cases: the result is resin pollution leaked, dripped onto the floor

o. the tool, roll, brush polluted with resin are not locked, waste is not stored suitably

p. during gobbling anti-sprinkling screen is not applied, drop cloud arises, the degree of exhalation increases

Conclusion

During the planning of every protection technique requirements must be set on the highest level. When it is not succeeded forcing styrene concentration below the admissible limit, only in that case is possible to apply the next, lower action level. This is particularly valid for the open-mold processing technologies, so in the cases of spraying, winding and manual laminating, when the resin is in permanent contact with environment contrasted with closed-mold technologies.

The main problem-causing factor of manufacture-style plants is the application of open-mold processing technologies. In order to standardize workflows and secure the environment and health protection producers have to choose closed-mold processing, with these the above mentioned open-mold processing technologies are replaceable.

In temperature relations of the degree of styrene evaporation the ambient temperature is a determining factor, has an effect to the imbibition speed of glass strengthening material, the conformation of glass-resin proportion, as the exhalation speed is directly proportional with the temperature rise.[2]

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2 The emission degree rises with 5 g/m² per 1C°. So e.g. it is 40 g/m²on 18C°, 100 g/m² on 30C°.

The ambient temperature at the processing place can show a great fluctuation in summer and winter periods, 10°C temperature rise can be followed by double-triple styrene emission compared with the original value.

By increasing wall thickness - applying the same initiator system – the heating and styrene emission rises at the same time.

Proposals

Workflows accompanied by high emission - e.g. gel spraying or laminating extra-large surfaces – have to be timed to the end of working days, when most of the workers have left the plant. Do not implement parallel several processes which are accompanied by styrene emission!

- The complete cross-linkage of moulded pieces should be finished in a separated, some cases tempered room (post-hardening). When the product hardens in a ventilated room, the apertures should be closed to reduce ventilation energy.
- The change of workers should be organized in a right time to minimize daily average styrene load. Every employee should get to know and learn the complete workflows.
- Employees should be aware that they are exposed to styrene effect even if they are working in conformity with prescriptions. Every operation with resins – first of all laminating and rolling processes – happens in the area between the person and the place of extraction (extractor head). E.g. rolling goes with permanent moving of resin surface, and during this resin drops spread into the air. The overall surface of these drops is quite large, so the styrene exhalation is also large. Practically each rotation of the roll is air-polluting.

  Therefore it is important for the employees to touch every breathing-in zone, and after pass along towards the piece under procession that towards aspiration channel. It should be controlled frequently that the employee works in conformity with these prescriptions.
- Tool allocation must be as close as possible to the exhaustion. This should be provided even if the worker does his job with moving around the tool or the tool rotating during procession. It is essential to provide fresh air breathing under any circumstances.
- During fibre spraying the filters in exhaustion channels can be stuffed by fibreglass, so the air resistance grows, the ventilation gets worse. These spare parts should be controlled or changed frequently. Proposed solution is to build in tilting filter cartridges, because in case off accidental full choking the channels can be opened manually easily.
- Doors and windows – especially the large ones - should be kept closed during workflows to block air turbulence and to stop getting out uncontrolled released styrene from workspace not to irritate neighbouring environment.

- As much thick-laying should be applied as possible in close succession (wet to wet), as the 80% of emission amount is coming from the top layer.
- Work should be done quickly and with permanent speed both at resin application and winding served for exhaustion and compacting. Resin should be catalysed that after finishing lamination the gelation should start immediately.

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