

Styrene use and occupational exposure in the plastics industry

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TOSSAVAINEN, A. Styrene use and occupational exposure in the plastics industry. *Scand. j. work environ. & health* 4 (1978): suppl. 2, 7—13. The commercial production of styrene was started in the 1930s. Currently 7 million tons of styrene a year is made worldwide by the catalytic dehydrogenation of ethylbenzene or by a process in which styrene is produced as a coproduct with propylene oxide. An estimated 62 % of the styrene monomer is consumed in the manufacture of polystyrene, 12 % in acrylonitrile-butadiene-styrene resins, 17 % in styrene-butadiene rubber and latex, 7 % in unsaturated polyester resins, and 2 % in other applications. Occupational exposure to styrene occurs in monomer production and polymerization plants, during the fabrication of plastic products from monomeric or partly prepolymerized styrene, and during the transportation and handling of liquid styrene. Due to unreacted residual monomer or thermal degradation of the polymer, low concentrations of styrene can be detected during the use of plastic products. The most extensive and intensive exposure occurs in the reinforced plastics industry, in which over 200,000 workers are exposed to a styrene concentration typically ranging from 20 to 300 ppm.

Key words: plastics industry, styrene.

HISTORICAL PERSPECTIVES

Styrene was discovered in 1827 by Bonastre during experimentation with alcohol extracts of *Storax* balsam (3). In 1831 he separated styrene as an oil-like distillate of the balsam. The chemical reaction during the distillation is a pyrolytic decarboxylation of organic acids. Otherwise styrene is not known to occur as a natural product. Its propensity to polymerize was observed in 1839 by Simon after he allowed styrene to stand in air (10). He also gave the name "styrol" to the hydrocarbon, which was prepared by steam distilling the saps of styraceous trees. In 1867 Berthelot synthesized styrene by passing acetylene and various

aromatic hydrocarbons through a heated porcelain tube (2). Later, in the beginning of the 20th century, styrene was detected as an impurity in industrial products such as coal tar, carburetted water gas, and effluents of petroleum cracking.

Although the methods for synthesizing and polymerizing styrene in the laboratory were discovered in the middle of the 19th century, its commercial production did not begin until 1925. The first process for producing styrene was operated by the Naugatuck Chemical Co. in the United States, but owing to many difficulties the manufacture was soon discontinued (7). At about the same time I. G. Farbenindustrie in Germany began development work which was carried through to a successful commercial conclusion. In 1930 the Dow Chemical Co. entered the styrene field and ultimately became the first com-

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pany in the United States to produce commercial styrene successfully.

The worldwide production of styrene has grown from less than 30,000 tons in 1938 to 2.5 million tons in 1965 and to about 7 million tons in 1977 (4, 11). For the period from 1965 to 1977 the demand for styrene had an average growth rate of 12 % a year, and the growth in demand is expected to continue at 6 % a year until 1981 (11, 13).

The expansion of monomer production facilities laid the groundwork for the development of polystyrene and styrene copolymers. In the 1930s styrene was mainly consumed in the synthetic rubber industry. In Germany the trademark was Buna-S, and in the United States styrene-butadiene copolymer was known as GR-S rubber. Styrene-butadiene rubber and tire production still account for about 10 % of styrene use, but in recent years the consumption of styrenic plastics, resins, coatings, and paints has increased considerably. The production of polystyrene has grown from a few thousand tons in 1937 to 4.2 million tons in 1977 (7, 16, 17, 18, 19). Unsaturated polyesters and reinforced plastics were introduced for military use in 1942 (12). The technology and industrial applications of glass reinforced plastics were mainly developed in the 1950s. Acrylonitrile-butadiene-styrene resin was introduced for the plastics market in 1948. To date no significant commercial uses of styrene based on chemical reactions other than polymerization or copolymerization have been developed.

PRODUCTION OF STYRENE MONOMER

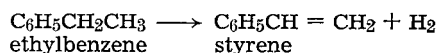
Styrene production is intimately interrelated with the coal tar and petroleum industries because of its large consumption of raw materials from these sources. The first step of the synthesis is a catalytic Friedel-Crafts alkylation of benzene with ethylene. Styrene production represents the greatest single use of benzene, approximately 50 % of world capacity, and the third greatest use of ethylene

Dehydrogenation process

Process steps

1. Alkylation of benzene with ethylene
2. Purification of ethylbenzene
3. Dehydrogenation of ethylbenzene
4. Purification of styrene

Reaction summary



Oxidative process

Process steps

1. Alkylation of benzene with ethylene
2. Reaction of ethylbenzene with oxygen
3. Reaction of ethylbenzene hydroperoxide with propylene
4. Recovery of unreacted propylene
5. Hydrogenation of unreacted ethylbenzene hydroperoxide to 2-phenyl ethanol
6. Recovery of unreacted ethylbenzene and propylene oxide
7. Dehydration of 2-phenyl carbinol to styrene
8. Purification of styrene

Reaction summary

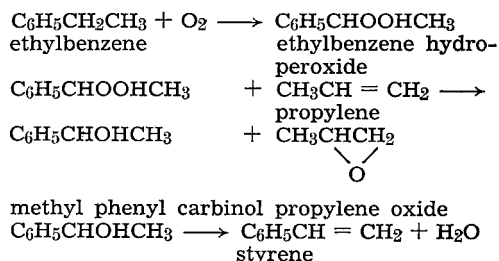


Fig. 1. Description of the styrene monomer processes.

next to polyethylene and polyvinyl chloride manufacture (11, 13). Historically benzene and ethylene have been the primary factors in determining the final styrene cost, but in recent years fuel has become more important.

Nowadays two competitive processes are used in styrene manufacturing. Both of the processes use ethylbenzene as their base. In the older process, high-purity ethylbenzene is catalytically dehydrogenated in the vapor phase to produce styrene (fig. 1). The oxidative process, in which styrene is produced as a coproduct with propylene oxide, was introduced in the 1970s in the United States, Japan and Spain (11). In this process ethylbenzene

is oxidized to its hydroperoxide, which is then reacted with propylene to yield propylene oxide and methyl phenyl carbinol. The carbinol is then dehydrated to styrene. Inhibitors such as sulfur and tertiary butyl catechol are added during the purification to prevent polymerization.

Table 1 shows the annual production of styrene monomer in the world. The United States, Japan and the Federal Republic of Germany are the major producers. The global distribution of styrene production has changed little since 1965, when the capacity and consumption was 2.5 million tons in comparison to 7 million tons in 1977. The pattern of the monomer production in 1965 was: United States 52 %, Federal Republic of Germany 12 %, Japan 8 %, United Kingdom 7 %, France 5 %, Italy 5 %, and others 11 % (4). The corresponding shares in 1977 were as follows: United States 41 %, Japan 16 %, Federal Republic of Germany 12 %, United Kingdom 5 %, Italy 5 %, France 4 %, and others 17 % (table 1). The other styrene-producing countries include Argentina, Australia, Brazil, Bulgaria, China, Czechoslovakia, the German Democratic Republic, India, Poland, Rumania, South Africa, the Soviet Union, and Yugoslavia (14, unpublished working paper of the International Agency for Research on Cancer). At the end of 1976 there were 11 styrene producers at 13 locations in the United States (11). Their annual capacity was 2.84 million tons. One plant used the oxidation process. Styrene has been produced commercially in Japan since 1959, and in 1976 nine companies manufactured monomeric styrene.

Table 1. Production of styrene (11, unpublished working paper of the International Agency for Research on Cancer).

Country	Year	Production (tons)
United States	1976	2,864,000
Japan	1976	1,090,000
Federal Republic of Germany	1976	860,000
United Kingdom	1976	340,000
Italy	1976	325,000
France	1976	270,000
Canada	1974	146,000
Spain	1976	60,000
Mexico	1974	30,000
Others	1976	approx. 1,000,000
World	1977	7,000,000

The world's styrene monomer markets are dominated by the giants of the chemical industry, for example, Dow, Monsanto, Borg Warner, Shell, ICI and BASF (14, 19).

USES OF STYRENE

An estimated 90 % of the styrene consumed in the world is used in the production of plastics and resins. The other 10 % is consumed in the synthetic rubber industry. In 1976 the end-uses of styrene were: polystyrene (PS) 62 %, acrylonitrile-butadiene-styrene (ABS) and styrene-acrylonitrile (SAN) resins 12 %, styrene-butadiene copolymers including styrene-butadiene rubber (SBR) and latex 17 %, and

Table 2. Pattern of styrene consumption (%) (11, 13, unpublished working paper of the International Agency for Research on Cancer).

Material	United States	Europe	Japan	World
Polystyrene	61	70	65	62
Acrylonitrile-butadiene-styrene + styrene-acrylonitrile resins	11	8	12	12
Styrene-butadiene copolymers	19	12	13	17
Polyester resins	7	7	6	7
Miscellaneous	2	3	4	2
Total	100	100	100	100

Table 3. Production of polystyrene (13, 16, 17, 18, 19, unpublished working paper of the International Agency for Research on Cancer).

Country	Year	Production (tons)
United States	1976	1,453,000
Japan	1976	582,000
Federal Republic of Germany	1976	470,000
France	1976	280,000
Italy	1976	260,000
United Kingdom	1976	215,000
Belgium	1976	190,000
Netherlands	1976	150,000
Spain	1976	85,000
Canada	1975	68,000
Brazil	1975	48,000
Mexico	1975	38,000
Finland	1976	20,000
Others	1976	approx. 350,000
World	1976	4,200,000

unsaturated polyester resins 7 %, and miscellaneous applications 2 % (table 2). The pattern of consumption is rather similar in the United States, Europe, Japan, and the rest of the world. In 1976 an estimated 4.2 million tons of polystyrene, 1.8 million tons of acrylonitrile-butadiene-styrene, 4.0 million tons of styrene-butadiene copolymers, and 2.0 million tons of reinforced plastics were produced worldwide (tables 3, 4, and 5). These materials represent approximately 20 % of all plastic sales and consumption (16, 17, 18, 19).

Table 4. Production of styrene-butadiene copolymers (13, 16, 17, 18, 19, unpublished working paper of the International Agency for Research on Cancer).

Country	Year	Production (tons)
United States	1976	1,072,000
Japan	1976	558,000
Federal Republic of Germany	1976	195,000
United Kingdom	1976	190,000
France	1976	185,000
Italy	1976	155,000
Brazil	1975	96,000
Canada	1975	91,000
Spain	1975	70,000
Others	1976	approx. 1,400,000
World	1976	4,000,000

Styrene plastics are used in the manufacturing of a wide variety of articles, both nondurable (such as food packaging and disposables) and durable (such as appliances, automobile and capital goods). Table 6 presents the American styrene market by ultimate application. The major markets are packaging, construction, and transportation.

OCCUPATIONAL EXPOSURE TO STYRENE

Monomer and polymer production

Occupational exposure to styrene occurs in monomer production and polymerization plants, during the fabrication of plastic products from monomeric or partly prepolymerized styrene, and during the transportation and handling of liquid styrene. Low concentrations of styrene can also be detected in the workplace air during the use of latex paints, polyester putties, or during the thermal decomposition of styrene plastics.

A worker's exposure in styrene production and polymerization factories is typically composed of occasional outbursts and leakages of reactors, tubing or other equipment. The average styrene concentration in these plants rarely exceeds 20 ppm (table 7). However, high short-term exposures are expected among the production and maintenance workers (18). Depending on the type of process, exposure during monomer production can include other gaseous contaminants, raw materials and intermediates such as benzene, ethylene, ethylbenzene, propylene, or propylene oxide (fig. 1). In polymer production butadiene, acrylonitrile, and organic solvents can also be present in the work environment.

Monomer production employs approximately 10,000 workers in 50 plants located in 20 countries. The estimated number of polymerization factories is over 200 and the production of polystyrene, acrylonitrile-butadiene-styrene, styrene-acrylonitrile, and styrene-butadiene copolymer resins employs 50,000 workers. In table 7,

in which the total number of styrene exposed is estimated, polymer processing stands for the fabrication of polymer products, for example, curing of styrene-butadiene rubber tires, extruding, molding, or hot-wire cutting of styrene plastics. In these operations styrene exposure is due to the unreacted residual monomer or thermal degradation of the plastics (5, 9). The estimation of occupational exposure to styrene (table 7) is based upon production and consumption data, as well as upon the environmental studies which have been made by the Institute of Occupational Health or which have been reported in the proceedings of this symposium or elsewhere.

Reinforced polyester industry

If the intensity or extent of occupational exposure to styrene is considered, the production of glass reinforced plastics is the most important branch of industry. The essential ingredients in commercial unsaturated polyester resins are a linear polyester compound such as glycol phthalate, styrene monomer (approx. 40 w-%), and inhibitors to retard polymerization until the resin is fabricated. During fabrication organic peroxides and cobalt compounds are added to regulate the exothermic hardening reaction. As much as 10 % of the styrene evaporates into the workplace air during manual laminating or spraying, and the worker is exposed to a styrene concentration typically ranging from 20 to 300 ppm (1,6). The exposure level is determined by the process of application, the amount of resin consumed, and the efficiency of workplace ventilation. The cleaning of tools and removal of spills with acetone or methylene chloride adds to the solvent exposure.

In the hand lay-up process, lamination is accomplished by the alternation of layers of liquid resin and fiber glass mat. A roller is used to expel air bubbles from the finished product. The styrene concentration in the breathing zone of a worker during lamination can be calculated by the equation:

$$C = C_0 + \frac{2 \cdot p \cdot Q}{v \cdot (A + 4X\sqrt{A})} ,$$

Table 5. Production of reinforced polyester (includes reinforcements) (13, 15, 16, 17, 18, 19).

Country	Year	Production (tons)
United States	1977	700,000
Japan	1977	230,000
Federal Republic of Germany	1976	108,000
France	1976	78,000
United Kingdom	1976	68,000
Italy	1976	49,000
Spain	1976	26,000
Sweden	1976	24,000
Finland	1976	16,000
Norway	1976	13,000
Denmark	1976	10,000
Others	1976	approx. 700,000
World	1977	2,000,000

Table 6. U.S. styrene market by ultimate application in 1976 (11). (Total consumption of styrene = 2.4 million tons)

Form of consumption	%
Packaging	20.9
Construction	11.5
Transportation	10.6
Housewares	8.8
Toys, recreational vehicles and boats	7.8
Appliances	6.4
Carpets and other textile products	5.8
Disposables	5.1
Electrical and electronic equipment	3.9
Paper products	2.8
Personal care	1.5
Furniture	1.5
Miscellaneous	13.5

Table 7. Occupational exposure to styrene.

Process	Number of workers involved	Typical exposure (ppm)
Monomer production	10,000	1—20
Polymer production (PS, ABS, SBR)	50,000	1—20
Reinforced plastics production	200,000	20—300
Polymer processing (PS, ABS, SBR)	1,000,000	0.01—1

where C = styrene concentration in the breathing zone, mg/m^3 ; C_0 = styrene concentration in general air, mg/m^3 ; Q = styrene consumption (approx. 40 % of the resin consumption), kg/h ; p = percentage of styrene evaporated (approx. 10 %); v = air velocity in the breathing zone, m/h ; A = surface area of the finished product, m^2 ; X = distance between the face and surface, m .

According to the equation, a worker's exposure can be controlled by general and local ventilation, by the evaporation properties, and by the amount of resin used (6). The distance X can also be changed, when proper tools and work practices are applied.

The production of unsaturated polyester resins consumes 7 % of the styrene monomer produced in the world (table 2). The glass reinforced plastics industry manufactures 2.0 million tons of various products. In Western Europe 30 % of the products are fabricated by hand laminating, 15 % of the products by spraying, and 55 % of the production is manufactured by automatic techniques. The major markets are transportation (cars, trucks), construction (sheets, pipes, tanks) and the marine industry (boats). The worldwide number of workers involved in the production is over 200,000 (table 7), and they are typically employed in small enterprises. In Finland, for example, the reinforced plastics industry employs 1,800 workers in 170 companies.

SUMMARY

Styrene and styrene plastics are indispensable to our modern world. Polystyrene and styrene copolymers have been widely used since the 1930s in industry and in everyday life. The consumption is expected to grow in the future.

Over 200,000 workers are daily exposed to airborne styrene concentrations which are known to be hazardous to their health. The most extensive and intensive exposure occurs in the reinforced plastics industry. More than one million workers are exposed to a detectable styrene concentration at their workplaces.

REFERENCES

1. BERGMAN, K. *Styrenexposition i plastbåtsindustri. I. Tekniskhygienisk studie* (Arbete och hälsa no. 3). Arbetskyddsverket, Stockholm 1977. 40 p.
2. BERTHELOT, C. Liebig's Ann. Chem. 141 (1867) 181. Cited in *Ullmanns Encyklopädie der technischen Chemie* (16. Band, Dritte Auflage). Urban et Schwarzenberg, München 1965, p. 464.
3. BONASTRE, M. J. Pharmac. Chim. 13 (1827) 149, 17 (1831) 338. Cited in *Ullmanns Encyklopädie der technischen Chemie* (16. Band, Dritte Auflage). Urban et Schwarzenberg, München 1965, p. 460.
4. FOERST, W. Styrol. In: *Ullmanns Encyklopädie der technischen Chemie* (16. Band, Dritte Auflage). Urban et Schwarzenberg, München 1965, pp. 460—476.
5. FRAZER, D. A. and RAPPAPORT, S. Health aspects of the curing of synthetic rubbers. *Environ. health perspect.* 17 (1976) 45.
6. KALLIOKOSKI, P. *Lujitemuoviteollisuus — ongelmallinen työympäristö* [The reinforced plastic industry — A problem work environment] (Työterveyslaitoksen tutkimuksia 112). Institute of Occupational Health, Helsinki 1976. 130 p.
7. KIRK, R. E. and OTHMER, D. F. *Encyclopedia of chemical technology* (vol. 13). Interscience Publishers, New York, N.Y. 1954, p. 146.
8. LORIMER, W. V., LILIS, R., NICHOLSON, W. J., ANDERSON, H., FISCHBEIN, A., DAUM, S., ROM, W., RICE, C. and SELIKOFF, I. J. Clinical studies of styrene workers: Initial findings. *Environ. health perspect.* 17 (1976) 171.
9. PFÄFFLI, P., ZITTING, A. and VAINIO, H. Thermal degradation products of homopolymer polystyrene in air. *Scand. j. work environ. & health* 4 (1978): suppl. 2, 22—27.
10. SIMON, E. Liebig's Ann. Chem. 31 (1839) 265. Cited in *Ullmanns Encyklopädie der technischen Chemie* (16. Band, Dritte Auflage). Urban et Schwarzenberg, München 1965, p. 460.
11. SLEETH, C. V. Styrene monomer, Petrochemicals outlook — 13. *Chem. eng. prog.* Nov. (1977) 31—35.
12. THE SOCIETY OF THE PLASTICS INDUSTRY. *Facts & figures of the plastics industry*, New York, N.Y. 1975.
13. VERCHIN, J. C. The outlook for benzene derivatives in Europe, Petrochemicals outlook — 14. *Chem. eng. prog.* Nov. (1977) 35—41.
14. —. Die Kunststoffindustrie der Welt. *Kunststoffe* 65 (1975) 500—553.
15. —. Polyesters, Supply status report no. 9. *Mod. plast. int.* 5 (1975): 1, 65—66.
16. —. Europe waits for a turnaround. *Mod. plast. int.* 8 (1978) 18—19.
17. —. Japan 1977: A persistent low-growth economy dictates new shifts in strategy. *Mod. plast. int.* 8 (1978): 1, 13—15.

18. —. Markets '78: Pinpointing the growth, *Mod. plast. int.* 8 (1978): 1, 43. 19. —. U.S. plastics sales data; 1977 vs. 1976. *Mod. plast. int.* 8 (1978): 1, 51—57.

QUESTIONS AND ANSWERS

Questions to Mr. TOSSAVAINEN

- Dr. RANTANEN: Can you forecast the future trends in (a) the production of styrene, (b) the consumption of styrene, and (c) the trend in the number of exposed workers?
- Mr. TOSSAVAINEN: For the period 1965 to 1977 styrene demand has grown 12 % a year. On a global basis, for the next four years the styrene consumption is expected to grow about 6 % a year [Sleeth, *Chem. eng. prog.* Nov. (1977) 31—35 and Verchin, *Chem. eng. prog.* Nov. (1977) 35—41]. Roughly speaking, the number of exposed workers will increase along with the expansion of styrene use.
- Prof. THIESS: Is it reasonable that styrene production will increase between 1978 and 1981 by 6 % per year — because the capacity of existing plants all over the world lies between 40 % and 70 %?
- Mr. TOSSAVAINEN: The operating rate for the installed monomer production plants would be about 70 % around 1980 [Verchin, *Chem. eng. prog.* Nov. (1977) 35—41]. New capacity will not be needed until the early 1980s.