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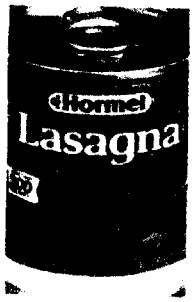

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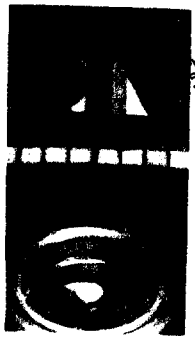

The cover: Break resistance of new barrier containers symbolizes a new era of plastics' dominance in packaging.

Low-styrene-emission laminating resins prove it in the workplace

By Leonard Walewski* and Steven Stockton*

New unsaturated polyesters with low styrene emission (LSE) levels significantly reduce employee exposure to monomer vapors in plants where ventilation is minimal and renovation impractical. In well-ventilated plants, LSE resins reduce styrene escape into outside air

SEVERAL evaluations in actual production environments prove that a new family of unsaturated polyester (UP) laminating resins provide significant reduction in styrene monomer emission levels while maintaining wetout characteristics and laminate physical properties equal to or better than those of conventional laminating resins (Table I). These low-styrene-emission (LSE) resins, introduced by USS Chemicals last year, permit a 20% reduction in styrene monomer content in the liquid resin.

Static laboratory screening tests (1)[1] in which the difference in weight between the liquid resin and the cured resin was determined showed that conventional UP resins emitted approximately 100 g./m.^{2} whereas the LSE resins emitted approximately 30 g./m.^{2} The procedure used for the screening test was as follows:

A circular disk mold (14.5 cm. in diameter) was weighed to the nearest 0.01 gram. 120 g. of resin was catalyzed and mixed for 1 min. Exactly 100 g. of catalyzed resin was then poured into the pre-weighed disk mold. After the resin gelled and the exotherm subsided, the disk mold was again weighed with the cured resin included. The difference in weight, in g., between the disk mold with the liquid resin and the mold with the fully cured resin was calculated to be the weight loss of styrene. Using a factor of 0.0165 m.^{2} for the surface area of the disk mold, the number of grams of styrene lost was converted to styrene emission in g./m.^{2} The tests, repeated many times, indicated that the LSE resins manifested a 60-70% decrease in emission levels.

The reason for interest in a high-performance LSE resin is a National Institute for Occupational Safety and Health (NIOSH) criteria for a recommended standard for styrene (2). It recommends the following standard for styrene: "Exposure to styrene in the workplace shall be controlled so that workers are not exposed to styrene at concentrations greater than 50 parts per million (p.p.m.), determined as a time-weighted-average (TWA) exposure concentration for up to a 10-hr. workshift, 40-hr. workweek. A ceiling concentration of 100 p.p.m. as determined during any 15-min. sampling period is also recommended."

This recommendation may lead to a requirement of significant capital investment for more adequate ventilation systems. Thus the economic significance of a high-performance LSE resin cannot be underestimated.

The new LSE resins have been tested in production environments. Monitoring was done to characterize worker exposures. This paper will discuss the in-plant monitoring procedures and compare results obtained with the LSE resin versus those of a conventional laminating resin.

Table I. Comparison of properties of conventional and low-styrene UP resins

Properties	Conventional resin	USS LSE resin
Styrene content	**44%**	**36%**
Brookfield viscosity at 77°F.		
No thixotrope, RVF-SP #1 at 20 r.p.m., cp.	170	175
With thixotrope, RVF-SP #2		
At 20 r.p.m., cp.	680	670
At 2 r.p.m., cp.	1900	2000
Thixotropic index	2.8	3.0
Cure behavior:		
Gel time at 77°F. with 1.25% MEKP, min.	23.7	22.6
Time to peak exotherm, min.	10.0	8.0
Peak exotherm, °F.	301	318
Physical properties of laminate[a]		
Flexural strength, p.s.i.	25,600	27,600
Flexural modulus, p.s.i.	712,000	689,000
Tensile strength, p.s.i.	15,900	17,200
Tensile modulus, p.s.i.	929,000	900,000
Elongation, %	2.5	2.6
Barcol hardness	45–50	45–50

a: Laminate ⅛-in. thick, 30% glass, made with 3 plies of 1.5-oz. glass mat.

In-plant exposure monitoring

Environmental conditions of testing. To show that the LSE resin would indeed help lower employee exposure to styrene, control over variables affecting environmental sampling was necessary. When monitoring for employee exposure levels, testing usually is relatively simple. However, it is difficult to isolate styrene emissions in a production environment.[2] The reason is that there is more than one styrene emission source in a plant. These sources, if unaddressed, could interfere with LSE resin testing.

In order to isolate the emission of styrene from the source being tested, the following conditions were met to the maximum extent possible:

1) Gel-coating operations were completed the day before environmental testing was done. Residual styrene in the plant air was then exhausted.

2) One full day of environmental testing was completed while the plant

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Based on a paper presented at the 1985 SPI RP/C Institute Conference in Atlanta.
1: Numbers in parentheses designate references at end of article.
2: Some field tests did not fully meet the criteria established for a properly run evaluation. The primary factor was lack of control over sources of styrene vapor. In one case, unrelated partially cured production parts were brought into the testing area to cure (and emit styrene vapor), resulting in a continually increasing "background" styrene concentration. In other cases, styrene-based products such as gel-coated parts were brought into the testing area, or improperly catalyzed material resulted in excessively long cure cycles. The results of these trials are not included in this paper.

was using a conventional laminating resin. Again, styrene in the plant air was exhausted before the next run.

3) One full day of environmental testing was undertaken while the plant exclusively used the LSE resin.

4) The same amount of each laminating resin was used on each day.

5) The same employees, performing the same routines, were monitored on each day of testing.

6) Gel time and cure time of each tested resin were the same.

Method of testing. A standard test method as outlined in the NIOSH Manual of Analytical Methods was used (charcoal tube method). The principle of the method is as follows:

A known volume of air is drawn through a charcoal tube to adsorb organic vapors (styrene). The charcoal in the tube is transferred to a small, graduated test tube and desorbed with carbon disulfide. An aliquot of the desorbed sample is then injected into a gas chromatograph. Lastly, the area of the resulting peak is determined and compared with the areas obtained from the injection of styrene standards.

Advantages of this method are:

1) The sampling device is small, portable, and involves no liquids.

2) The charcoal tubes are analyzed by a quick instrumental method.

3) Simply by changing gas chromatographic conditions, the method can be used for simultaneous analysis of two or more solvents suspected to be present in the same sample.

One disadvantage is that the amount of sample is limited by the weight of contaminant which the tube can hold. The possibility of sample loss exists should the tube become overloaded. Therefore, to avoid overloading tubes with styrene vapors, the sampling period was limited to no more than half of a normal workshift. When performing environmental testing for an entire shift (8 hr.), sample tubes were changed at mid-shift.

An approved personal sampling pump calibrated to 100 cc./min. was used for personal as well as area samples. The glass sample tubes, constructed with both ends flame-sealed, were 7 cm. long with a 6 mm. OD and a 4 mm. ID. Each contained two sections of 20/40 mesh activated charcoal separated by a 2-mm. portion of urethane foam. The adsorbing section contained 100 mg. of charcoal and the backup section 50 mg. Sealed ends of each tube were broken immediately prior to each sampling period, and capped immediately after sampling.

Environmental testing

Semi-production environment. The initial evaluation of styrene exposures was made in a semi-production environment. Table II shows an overall reduction of styrene exposure levels of 39% when using the LSE resin. Production-type chopper/spray equipment was used in a large spray booth. Exposure levels in Table II are very high because no ventilation was used during the test.

We were unsuccessful in attempting to evaluate the difference between standard resin and LSE resin in the spray booth with the ventilation system on. Ventilation was too efficient to enable significant detection. Average exposures with the ventilation system on for both resins were under 9 p.p.m. In trials with the ventilation system off, it became clear that using LSE resin results in lower styrene exposures.

Boat manufacturing. Table III lists the occupational exposures to styrene in actual production environment in the marine industry. A full day of environmental testing was done with employees in a Florida plant, using a standard resin. Their average exposure to styrene was close to 120 p.p.m. Under the same testing conditions, when using the LSE resin, the same employees were exposed to an average of 50 p.p.m. of styrene vapors. The overall reduction in exposure was 54%. Table III also shows occupational exposures to styrene in a California production environment. The overall reduction in styrene exposure using LSE was 31%.

Table II Personnel styrene exposure in a semi-production environment (laboratory conditions, production equipment)

Worker occupation	Styrene exposure[a], p.p.m. Standard resin	LSE resin	Reduction, %
Operator	225	143	36
Roller	27[b]	101	–
Roller	227	124	45
Area sampler	210	135	36
Average reduction			39

a: Estimated employee 8-hr. time-weighted-average styrene exposure in parts of styrene/million parts of air, assuming employees worked at the pace they were working for an entire shift.
b: This result is unrealistically low, probably due to pump failure; thus result is not used in calculation of the average % reduction in styrene exposure.

Table III Personnel exposure to styrene in boat manufacturing

Worker occupation	Styrene exposure[a], p.p.m. Standard resin	LSE resin	Reduction, %
Florida plant			
Hull gun runner	113.2	64.0	43.5
Gun runner 1	158.2	37.7	76.2
Gun runner 2	108.0	69.6	35.6
Gun runner 3	80.3	43.9	45.3
Roller 1	140.1	38.4	72.6
Roller 2	85.1	43.6	48.8
Roller 3	131.2	56.9	56.6
Average reduction			54.1
California plant			
Foreman (chopper)	30	7	77
Chopper 2	106	77	27
Chopper 3	41	47	(15)[b]
Roller 1	75	37	51
Roller 2	61	40	34
Roller 3	56	42	25
Area sampler 1	18	12	33
Area sampler 2	19	4	79
Area sampler 3	9	13	(44)[b]
Area sampler 4	30	16	47
Average reduction			31.4

a: Each result is the occupational 8-hr. time-weighted-average exposure.
b: Increase.

References

1) SPI RP/C Inst. 39th Annual Conf. Preprint Book, paper 6-D, "Reducing the styrene emission of polyester laminating resins," G. Luong and L. Walewski, USS Chemicals (1984).

2) "Criteria for a recommended standard...occupational exposure to styrene," U.S. Department of Health and Human Services, Public Health Service; National Institute for Occupational Safety and Health (NIOSH), Sept. 1983.

3) "NIOSH manual of analytical methods" 2nd Ed., Vol. I, Feb 1977. ■