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Health Aspects of the Curing of Synthetic Rubbers

by David A. Fraser* and Stephen Rappaport†

A commonly used tread rubber formulation was cured in the laboratory under conditions simulating vulcanization in the Bag-O-Matic press. Volatile emissions were collected on charcoal and analyzed by combined GC-mass spectrometry. The compounds identified were either contaminants present in the raw material or reaction products. Some of these compounds were also identified in charcoal tube samples collected in the atmosphere of the industrial operations. Estimates based on the loss of weight of rubber during curing were used to predict airborne concentrations and compared to the concentrations actually found. The literature of the toxicity of raw materials and effluents was reviewed, and no acute or chronic toxicological effects would be anticipated. Information concerning potential carcinogenicity was not available and could not be evaluated.

For the past four years the Occupational Health Studies Group at the University of North Carolina has been studying the health of workers in the rubber industry. One aspect of this study has been an attempt to characterize the environment of the worker and to measure the exposure to the myriad of chemicals used in the industry. It was soon evident that little was known of the chemical nature of the fumes produced during the curing operation. It was also clearly impossible to investigate each of the hundreds of formulations that are used in the industry for special products or purposes. One recipe which was considered to be typical and to account for the major production of bias-ply tread stock was chosen for study both in the laboratory and under field conditions. This formulation was mixed by a major manufacturer and shipped to us in sheets ¼ in. thick and 1 ft square. These were stored in a freezer until used in the laboratory studies. Samples of each of the ingredients used were also provided.

Estimating Potential Emissions

Curing emissions will be discussed from two vantage points: first, the phenomenon of volatilization, whereby components of the curing system are lost through physical processes, and second, the possibility that volatile substances may be generated by chemical interactions.

Physical Losses

The diversity of ingredients of the uncured stock has been emphasized. Of these organic constituents, several have sufficient vapor pressure at process temperatures to be liberated from the rubber matrix. This volatilization has been observed (*1*) to obey the equation:

$$C = C_0(1 - e^{-mt/R})$$

where C is the amount of ingredient lost in time t as percent by weight of rubber, C_0 is the initial content ($t = 0$) of the ingredients in the rubber as percent of weight, m is a constant which is a function of the diffusion coefficient of the ingredient at process temperature, R is the thickness of the stock, and t is the time at the process temperature. Thus, physical losses of particular ingredients are related exponentially to the temperature and duration of cure, stock thickness, and individual diffusion coefficients.

Since vapor pressure data for most technical compounding ingredients are unavailable, it is impossible to predict exact emissions at process temperatures. However, the literature reviewed indicates that losses occur primarily among ingredients which are either liquids at room temperature or solids with melting points at or below curing temperatures (*1–10*).

Polymer or Blend Volatiles. General purpose polymers maintain their integrities in the

* Department of Environmental Sciences, University of North Carolina, Chapel Hill, North Carolina 27514.

† Los Alamos Scientific Laboratory, Los Alamos, New Mexico 87544.

presence of heat until pyrolysis temperatures (200–400°C) are reached. Only upon continued heating at 175–225°C for several hours have depolymerization processes been noted (*2*). Curing operations of shorter duration should result in little or no breakdown. Polymeric losses will, therefore, be a result of residual amounts of monomer and impurities from manufacturing processes and should represent less than 1% of polymer on a weight basis. A list of the polymers most commonly used in the rubber industry is given in Table 1.

Table 1.

General-purpose polymers	
Natural rubber	NR
Polyisoprene	IR
Styrene–butadiene rubber	SBR
Isoprene (Butyl) rubber	IIR
Polybutadiene	BR
Ethylene–propylene terpolymer	EPDM
Acrylonitrile–butadiene (nitrile) rubber	NRB
Special purpose polymers	
Polychloroprene	CR
Chlorosulfonated polyethylene	CSM
Fluorocarbon	FPM
Silicone rubber	

Monomers are sufficiently volatile to be lost appreciably in prevulcanization milling and calendering operations, e.g., styrene, bp 145°C; acrylonitrile, bp 78°C; chloroprene, bp 59°C. Thus, the extent to which they are present at the curing stage cannot be predicted.

Antioxidants and Antiozonants. Studies designed to determine the extent of volatilization of antidegradants from compounded stocks (*1*, *4*, *11*) have led to the following conclusions. In most cases, heating losses of phenolic compounds are higher than for their amine counterparts. Furthermore, losses are inversely proportional to stock thickness and greater in black stocks than gum. Overall, total discharges from curing molds may range as high as 5–20% for thin stocks and for the more volatile antidegradants. However, normal vaporization in curing rubber generally results in a weight reduction of 0.5–0.1% of antidegradant present. Table 2 lists some common antidegradants with their melting points.

Accelerators. As with antidegradants, common accelerators have melting points in the range 70–200°C. Thus, some less at curing temperatures would be expected. Some common accelerators are listed in Table 3.

Table 2. Melting points of common antidegradants.

Type	Compound	Melting point, °C
Phenol	2,6-Di-*tert*-butyl-4-methylphenol	69–70
Phenol	2,4-Di-*tert*-amylphenol	Liquid
Phenol	3-*tert*-Butyl-4-hydroxyanisole	Liquid
Phenol	2,2′-Methylene-bis (4-methyl-6-*tert*-butyl phenol)	125–130
Amine	Phenyl-β-naphthylamine	105–106
Amine	*N,N′*-Diphenyl-*p*-phenylenediamine	144–152
Amine	*N,N′*-Diphenylethylenediamine	60–65

Table 3. Melting points of common accelerators.

Type	Compound	Melting point, °C
Dithiocarbamate	Zinc diethyldithiocarbamate	171–180
Dithiocarbamate	Zinc dibutyldithiocarbamate	98–108
Dithiocarbamate	Sodium dibutyldithiocarbamate	Liquid
Dithiocarbamate	Selenium dimethyldithiocarbamate	140–172
Thiuram	Tetramethylthiouram monosulfide	103–108
Thiuram	Tetramethylthiouram disulfide	140–148
Thiuram	Tetraethylthiuram disulfide	62–75
Sulfenamide	*N,N*-Diethyl-2-benzothiazylsulfenamide	Liquid
Sulfenamide	*N*-Cyclohexyl-2-benzothiazylsulfenamide	93–108
Sulfenamide	*N*-Oxydiethylene-2-benzothiazylsulfenamide	70–90
Thiazole	2-Benzothiazyl-*N,N*-diethylthiocarbamylsulfide	164–176
Thiazole	Benzothiazyl disulfide	160–176
Thiazole	2-Benzothiazyl-*N,N*-diethylthiocarbamylsulfide	69
Guanidine	Diphenylguanidine	145–147
Guanidine	Di-*o*-tolyguanidine	167–173

Processing Aids, Diluents. Processing aids generally take the form of oils, usually paraffinic, and function as lubricants, plasticizers, and softeners. Diluents are primarily extender oils of aromatic character used to improve performance of synthetic rubbers. Volatilization from these crude mixtures will vary considerably. Overall, volatiles lost in 3 hr. at 167°C, range from 0.05 to 1.0% of the total weight (*3*).

Miscellaneous Compounding Ingredients. In addition there are many ingredients which may be added to a formulation to achieve specific results. Of these, the vulcanizing agents and retarders are most likely to be volatilized at process temperatures. These substances include amines, esters, and organic acids. In most cases they are either liquids at room temperature or solids with melting points between 70 and 200°C (*12, 13*). Losses of 1% might be expected.

In virtually every case the materials incorporated in the formulations are of technical grade. Thus, the purity of the main isomer or ingredient is low (60–95%), and some impurities will possess sufficient volatility to be released. One indication of relative purity levels is the wide melting ranges of the ingredients. One antitoxidant marketed under at least eight trade names is a "high temperature reaction product of diphenylamine and acetone." The reagents used in its production are of commercial grade. Thus from this single ingredient trace amounts of hundreds of impurities may be emitted into workroom air. Gas chromatographic analysis of commercial antioxidants has confirmed these high levels of impurity (*14*).

Formation of New Compounds

The vulcanization process can be visualized as two distinct reaction periods. The first stage begins upon exclusion of air, and heating. The environment within the press is reducing, and upon opening, reduction products may be released as vapors and particulates.

Opening of the press initiates the second reaction period, whereupon hot rubber and ingredients, having migrated to the surface, are exposed to air. This oxidative stage will last for the life of the product, but is most critical when the freshly cured stock is still hot. Reactions may take place at this time and compounds may be lost either by volatilization or by physical forces which remove surface contaminants as particles.

Because so many reaction products are possible, it is difficult to predict the identities of those released. Furthermore, the presence of impurities suggests many minor reaction products which may be released as trace contaminants. For those reasons a general description of compound classes will be discussed rather than specific structures.

Amines and Ammonia. Sources of these compounds include sulfenamide, thiuram sulfide, dithiocarbamate, and guanidine accelerators, and interactions involving antidegradants and retarders. Amine reaction products would be likely to be volatilized during curing.

Organic Sulfides. The formation and emission of organic sulfides is both likely and unpredictable. Due to the interplay of ionic and free radical mechanisms, many products could result from a given mixture. Likely contributors from crosslinking reactions include accelerator fragments, mercaptans, and hydrogen sulfide.

Hydrocarbons, Acids, Esters. Formation of these compounds could occur as a result of free radical reactions involving polymeric alkyl groups. The interactions of rubber peroxy radicals and antioxidants may produce acids, esters, etc. Similar reaction products might be expected from oxidative processes in air.

Water and Steam Distillation. Water is both a major reaction product and a contaminant from many of the ingredients. Thus the possibility of steam distillation whereby high boiling materials are removed from the matrix exists. Many compounds such as organic acids which would not normally be volatilized might be removed in this way.

Passenger Tire Systems

Passenger tires are composed of many stocks but since volatilization is proportional to surface area, it is reasonable to assume that tread and sidewall stocks would be the major contributors to the evolution of volatile contaminants. It is possible to make a rough estimation of the amount of volatile matter released into workroom air from a hypothetical curing press. If we assume that a tire of stock formulation has a combined weight of tread (90%) and sidewall (10%) of 10 kg and further

assume that each ingredient of sufficient vapor pressure contributes a maximum of 1% of its formulation weight to losses from all physical and chemical processes, the total amount of volatile material released could be between 0.5 and 0.7% by weight (65 g). Of this amount the majority (90%) would be derived from the polymer or blend. Antidegradants would contribute approximately 5% of the losses, and accelerators roughly 1%. Note that the synthetic rubbers discharge approximately three times as much of the accelerator fraction as the natural rubbers. The remaining 3% of the emissions come from a mixture of oils and special additive ingredients.

To appreciate the number of compounds represented by this 65 g of material, the following assessment might be helpful. Of the two stocks per tire considered to contribute the majority of substances, there are at least 10 ingredients per stock which could be volatilized. Considering the assay of these technical ingredients, it would be a conservative estimate to say that 50 volatile compounds are present per ingredient. Thus the total number of compounds that may conceivably be released would be 1000.

Toxicological Implications

Since the amount of emissions of individual compounds is relatively small and acute effects have not been observed among employees, only the chronic hazard potential will be considered.

Polymer or Blend

No ill effects from chronic exposures to low concentrations of general purpose monomers have been reported (*15–17*). The estimated threat from volatilization of small amounts of these ingredients would have to be regarded as minor. However, with the recent developments concerning vinyl chloride, monomers and related compounds may have to be reevaluated with regard to carcinogenesis. A recent report has suggested an increased incidence of leukemia among workers using styrene–butadiene rubber.

Antidegradants

The antidegradants represent the most interesting class of ingredients from the standpoint of chronic effects. Though noncarcinogenic problems have been reported, some of the data suggests that the primary threat could be the induction of malignancies.

Noncarcinogenic Effects. Several papers have reported systemic effects induced by chronic exposures to antidegradants (*9–13, 18–30*). The method of action varies and includes liver, kidney, and lung impairment. Whether or not exposure concentrations in vulcanization areas are high enough to produce such remains to be determined.

Another problem commonly encountered in conjunction with antidegradants, especially the phenylenediamines, is that of sensitization (*22*). There are implications that both contact and systemic sensitization are possible. Since these phenomena are largely a function of individual susceptibility, an extremely low exposure to the sensitizer may trigger a response.

Carcinogenic Effects. Of the antidegradants in common use, the amines, nitrosamines, and quinolines may be suspect with regard to the induction of cancer. At least some members of these compounds classes have been shown to produce tumors in animals (*22, 27, 30*).

The method of action of these contaminants is not known, but current speculation (*31–37*) holds that the potential carcinogen or precarcinogen requires metabolic modification to become the causative agent. It enters the body and because of limited reactivity finds its way into cellular structures whereupon it is transformed through biochemical pathways into the ultimate carcinogen usually a strong electrophile (*27, 38*). It is important to realize that since the precarcinogen is presumably transformed in the body; it is possible that the eventual malignancy may appear in a site far removed from the point of entry. Thus even though the compound is inhaled, the tumor itself may be found in the kidney, bladder, or liver. Some recent epidemiological studies of rubber workers seem to confirm this suspicion (*39, 40*).

Without additional information regarding actual exposures in the curing area, it is not feasible to predict the possibility of specific cancer production. However, the potential for such interactions from antidegradant discharges is present.

Accelerators

The accelerators as a class present a possible exposure risk. Some systemic effects, including

liver changes, have been recorded, as have reports of dermatitis from several classes of primary accelerators and sensitization from amine secondary accelerators (*40–44*). An exposure which might be meaningful is related to the use of dithiocarbamates. The carbamates as a class and selenium diethyldithiocarbamate specifically, have been reported as potential carcinogens of the lung and hematopoietic organs. Amines associated with the use of accelerators are also potential carcinogens. For example, morpholoine (a breakdown product of the popular accelerator, *N*-oxydiethylene-2-benzothiazylsulfenamide) has been shown to induce tumors in animals (*31, 33, 34*) possibly the result of *in vivo* nitrosation reactions.

Miscellaneous

Of the remaining ingredient classes, several have been linked with carcinogenesis. In one reported case, 3,4-benzpyrene, a known lung carcinogene, was collected in a curing room in concentrations between 0.2 and 0.5μg/m^3 of air (*43*). Its presence was attributed to hardcoal tar (utilized in a high-pressure-reclaim rubber) which had been added to the stock. Many retarders are *N*-nitroso compounds and as such as suspect as carcinogens.

It has long been known that polycyclic aromatic hydrocarbons (PAH) are associated with carbon blacks (*45–47*). It is, however, unlikely that these high-boiling nonpolar molecules would be volatilized and lost at curing temperatures, since they are bound by strong absorptive forces to the particles.

Experimental Observations

The formulation used in the laboratory studies (*47*) is shown in Table 4. A 50–g piece of uncured stock was placed in a stainless steel vessel, which was purged with nitrogen and sealed with shut-off valves. Free of air, the chamber was heated in an oven to simulate the true press-closing and vulcanization stages. As the stock cured over a 20-min. period, volatiles were released from it and retained in the closed system. The vessel contained 47 mm absolute glass filters at both inlet and outlet to prevent particulate matter from contaminating the system.

Following the curing stage, the microvolume valve was switched to the alternate position and the oven was turned off. The vessel was slowly cooled and concurrently purged with 70 ml of air/min to wash the effluent into an adsorptive device downstream. Activated charcoal was selected as the absorbent because of its high collection efficiency for organic compounds, the ease of solvent desorption, and its insensitivity to water. This portion of the cycle was analogous to the actual press-opening and cooling stages, and lasted 30 min during which the organic fraction consisting of C_6 and above was retained. The adsorbent trap consisted of stainless steel tubing 80 mm × 6.5 mm I.D., containing 200 mg of 80/100 mesh activated coconut charcoal held by silane-treated glass wool plugs.

Individual compounds were separated by gas–liquid chromatography utilizing a gas chromatograph equipped with flame ionization detectors. The desired separation was achieved by temperature programming the column from 50 to 160°C at 2°C/min and from 160 to 330°C at 6°C/min, while inlet and detector tempera-

Table 4. Formulation of stock used in this investigation.

Ingredient	% by weight (approximate)
Polymer	
Styrene–butadiene rubber (1)	25
Styrene–butadiene rubber (2)	25
cis-Polybutadiene rubber	10
Antidegradant	
N-Phenyl-*N'*-*sec*-butyl-*p*-phenylenediamine [a]	0.5
Accelerator	
N-*tert*-Butyl-2-benzothiazole sulfenamide [b]	0.5
Diphenylguanidine	0.1
Oil	
Aromatic (total[c])	20
Carbon black	
Furnace black	30
Miscellaneous	
Sulfur	0.5
Activated zinc oxide	0.5
Stearic acid	0.5
Sunproof wax	0.5

[a] Trade name, Flexzone 5L.

[b] Trade name, Santocure NS.

[c] Since some oil is used to extend the SBR's, the figure shown here is the total weight % for all oils; this brings the total to greater than 100%.

tures were maintained at 200°C. Gas flow rates were 30, 35, and 400 ml/min for the carrier gas (He), hydrogen, and air, respectively.

Identifications were obtained (*47*) from combined gas chromatography–mass spectrometry and were based upon interpretation and/or comparison of mass spectra with standard spectra, upon comparison of gas chromatographic retention times with those of analytical standards, and upon an estimation of the compound's boiling point (derived from the gas chromatogram) and comparison with the known value. The same column was used as previously though the temperature program was terminated at 180°C to prevent excessive contamination of the MS detector.

The gas chromatogram obtained from the curing volatiles is shown in Figure 1. The compounds identified are listed in Table 5. A reconstruction of the chromatogram based on the identification and quantification by the mass spectrograph is shown in Figure 2. Samples were collected in the workplace and some of these compounds were identified (Table 6).

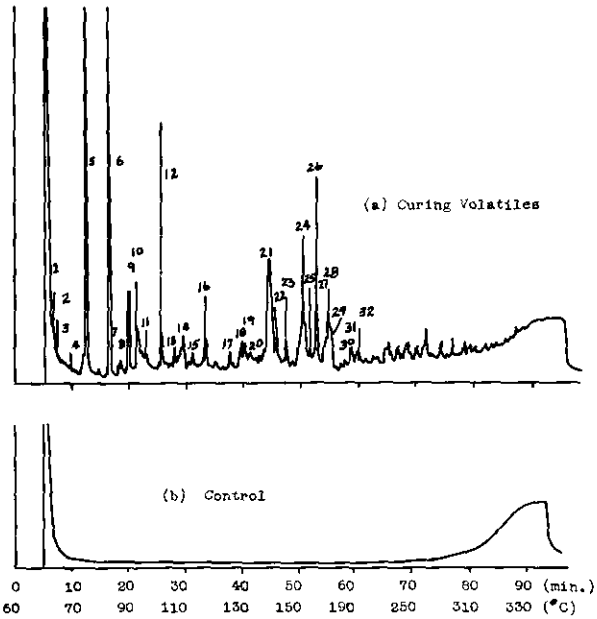

FIGURE 1. Gas chromatograms: (top) obtained from curing volatiles; (bottom) control.

Conclusions

The compounds identified are indeed a strange assortment. The oligomers of 1,3-butadiene, for instance, are quite abundant, especially the dimer, 4-vinyl-1-cyclohexene, which is primarily responsible for the characteristic odor of the stock. Other known oligomers present include 1,5-cyclooctadiene (dimer) and

Table 5. Compounds identified in the stock effluent.

Peak no.	Compound	Method of identification [a]	Probable source
5	Methylbenzene	MS + GC	*cis*-Polybutadiene rubber
6	4-Vinylcyclohexane	MS + GC	*cis*-Polybutadiene rubber
7	Ethylbenzene	MS + GC	Aromatic oil
8	Dimethylbenzene (1,3-and-1,4-)	MS + GC	Aromatic oil
9	Styrene	MS + GC	Styrene–butadine rubber
10	*tert*-Butyl isothiocyanate	MS + BP_{est}	*N-tert*-butyl-2-benzothiazole sulfenamide
11	1,5-Cyclooctadiene	MS + GC	
22	Benzothiazole	MS + GC	
23	*N-sec*-Butylaniline	MS + GC	*N*-Phenyl-*N'*-sec-butyl-*p*-phenylenediamine
24	1,5,9-Cyclododecatriene	MS + GC	*cis*-Polybutadiene rubber
25	Methylnaphthalene	MS + GC	Aromatic oil
26	1,5,9-Cyclododecatriene	MS + GC	*cis*-Polybutadiene rubber
27	1,3-Butadiene trimer	MS + BP_{est}	*cis*-Polybutadiene rubber
28	1,3-Butadiene trimer	MS + BP_{est}	*cis*-Polybutadiene rubber
29	1,3-Butadiene trimer	MS + BP_{est}	*cis*-Polybutadiene rubber
30	Ethylnaphthalene	MS + GC	Aromatic oil
31	Dimethylnaphthalene	MS + BP_{est}	Aromatic oil
32	Dimethylnaphthalene	MS + BP_{est}	Aromatic oil

[a] MS = mass spectrometry; GC = gas chromatographic retention time; BP_{est} = estimation of boiling point from gas chromatogram.

Table 6. Air concentrations of selected compounds.

Compound	Location [a]	Concentration, ppb [b] 1	2	2	4	5	6	7	8	9	Mean	Std. Dev.
Toluene	1	1500	1290	1190	887	992	1530	1240	832	660	1120	301
	2	1000	747	1210	1460	1240	1340	1130	1180	1140	1160	202
4-Vinyl-1-cyclohexene	1	84.5	97.7	66.1	56.0	70.6	77.7	71.6	60.6	54.4	71.0	8.42
	2	118	84.7	112	117	62.6	74.3	77.3	90.3	94.3	92.3	19.9
Ethylbenzene	1	81.6	126	69.0	53.4	82.8	90.0	86.6	60.5	53.8	78.2	22.7
	2	121	99.0	121	178	79.7	88.9	101	118	98.0	112	28.8
Styrene	1	96.3	130	79.4	61.5	83.2	86.7	95.6	67.5	61.6	84.6	21.5
	2	118	110	130	146	76.5	93.0	101	114	108	111	20.2
1,5-Cyclooctadiene	1	8.19	7.74	5.95	4.88	7.08	6.39	7.37	4.61	4.22	6.29	1.44
	2	6.08	4.56	7.33	8.84	5.58	6.34	6.42	6.55	6.35	6.45	1.17
1,5,9-Cyclododecatriene	1	8.68	8.64	5.68	5.86	8.37	7.13	9.22	5.61	5.70	7.21	1.52
	2	16.4	17.2	26.5	14.8	10.6	14.8	10.3	16.2	15.4	15.8	4.70

[a] Location 1 directly in center of passenger tire curing area; location 2 at periphery of passenger tire curing area.
[b] Nine samples were collected at each location.

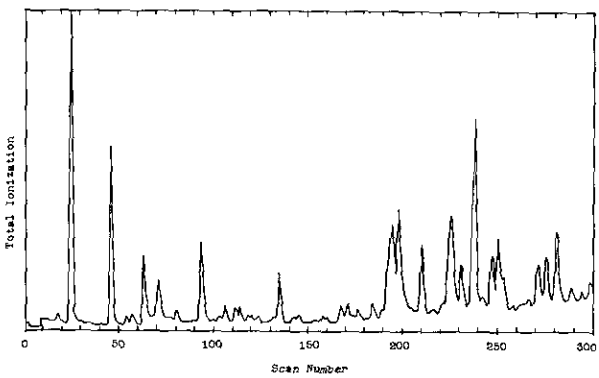

FIGURE 2. Reconstructed chromatogram of effluents based on quantification by mass spectra.

the 1,5,9-cyclododecatriene trimers. Peaks 27, 28, and 29 are thought to be butadiene trimers, although exact structures cannot be assigned. The general appearance of the spectra (especially the molecular ion at m/e 162) and the probable *cis*-polybutadiene rubber source of the compounds indicate this to be the case.

The presence of toluene was also confirmed and represents the largest peak resolved (peak 5). Though its particular spectrum is common of other C_7H_8 hydrocarbons, the GC retention times match perfectly. Again the ultimate source within the stock appears to be the *cis*-polybutadiene rubber.

Other compounds that were confirmed include styrene (residual monomer from the styrene-butadiene rubbers), *N-sec*-butylaniline (an impurity from the antiozonant), benzothiazole (from the accelerator), and several alkyl benzenes and naphthalenes (probably from the aromatic oil). One compound, *tert*-butylisothiocyanate, though not confirmed (standard unavailable) was tentatively identified from its mass spectrum and supported by other evidence including the estimated boiling point of the peak.

The results show that an unusual assortment of compounds are discharged during cure. With regard to volatility, both laboratory and field procedures point to low boiling compounds as being orders of magnitude more prevalent than the high boiling components.

Compounds identified in the effluent from the isolated tread stock included styrene, butadiene oligomers, alkylbenzenes and naphthalenes, and several specific nitrogen and sulfur-containing substances.

The presence of several of the compounds, principally the butadiene oligomers, was confirmed in field samples collected in the tire plant. However, chromatograms of charcoal tube eluates revealed a substantial number of peaks in the field sample that were not identified in the tread effluent. Judging from their low boiling points, these might be solvents

used in binding cements and/or volatiles from chloroprene rubber in the sidewall stock.

Other vulcanization processes would probably discharge a similar mixture though specific differences could exist. The loss of residual monomer and impurities, principally oligomers, would be expected in most cases. Impurities from accelerators, antioxidants and antiozonants (and related ingredients), and oil hydrocarbons would also be expected. In addition, bonding agents, cements, etc. might contribute to the effluent.

The primary substances discharged appear to be those arising from heating of compounding ingredients. The largest source of volatiles in the stock is the polymer or blend which also represents the bulk on a weight basis. Contributing but in lesser amounts are accelerators, activators, antidegradants, and oils. It is significant that for the tread stock analyzed all identified compounds were either all impurities or decomposition products. Parent compounds evidently did not possess sufficient vapor pressures to be lost to any extent. Nonstock ingredients of course may also discharge volatiles when heated. Most likely sources are bonding agents which thermally decompose or cements containing organic solvents.

Table 6 gives the range of concentrations for organic vapors found within the press room. Because of the uniformity between tire plants which utilize the Bag-O-Matic presses values obtained are probably representative. Thus, concentrations of individual substances between 0.005 and 2.0 ppm may be considered typical.

The upper end of the range (1–2 ppm) contains the more volatile compounds, i.e., in the C_5 to C_8 boiling point region such as toluene and styrene. Between C_8 and C_{10}, concentrations drop to roughly 1/10 of this level and above C_{10} are in the low ppb region. Instantaneous exposure levels may be higher (i.e., immediately upon press opening) but are undoubtedly of short duration. For the stock and process under study it is reasonable to assume that the ambient environment in the curing area is not overtly hazardous. Concentrations are so low that acute toxicity problems seem unlikely. The possibility that chronic exposures may result in disease manifestations is also questionable. However, since few data have been published concerning the chronic toxicities of most compounds identified (especially with regard to carcinogenesis and sensitization), the possibility of significant health effects cannot be ruled out.

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