Nitrogen and sulfur compounds in the working environment in rubber industry

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Introduction

Rubber industry is a very important branch of the national economy. The products of this industry are widely used in many production sectors/areas: motor-car industry, transport, power industry, mining, light industry, food industry. The production of rubber products involves complex operations and processing from a rubber mixture to a rubber product. The process of obtaining rubber products consists of the following steps:

- storage and raw materials handling,
- preparing a rubber mixture,
- factory lumber created/ creation?, component assembly and building,
- vulcanization
- control and finishing storage and distribution.

Production of rubber products is characterized by the emission of pollutants which are hazardous and harmful for health. The kind of this contamination depends on: the technological process, the way of vulcanization and the kind of materials used. It is estimated that during the processing of rubber compounds, a few hundred of chemical compounds which have different chemical, physical and toxic properties, are emitted to the air. Their concentration value can range from several nanograms to a dozen or so milligrammes in a cubic metre of air. Air pollutants are volatile components of materials used for preparing rubber compounds and chemical substances which are formed during processing of rubber compounds, particularly in a curing process. *Such compounds as aromatic and aliphatic hydrocarbons, organic and inorganic compounds of nitrogen, sulphur and oxygen have been identified in air sampling.* Compounds of nitrogen, like amines, nitrosamines, nitryls, isocyanates, amides, carbamates are made up 9.3 % of vulcanizing smoke and sulphur compounds, like sulphides, mercaptans, polysulfidy, thiols, thiurams – 33.6 %.

The aim of the tests was to identify nitrogen and sulfur organic compounds which are found in workplace air during production and processing of rubber compounds. The tests were carried out in three rubber industry factories producing rubber plates and forwarding tapes. The type of production is shown in Table 1.

Table 1. The type of production in the investigated plants.

Plant	Articles
A	rubber lining, seal plates, floor covering, dielectric mats
B	conveyer belts, rubber plates, rubberized fabrics
C	conveyer belts, rubber plates, elements of road engineering, industrial facings

Conditions of tests

In order to identify pollutants, air samples were taken using a stationary method. Samples were taken in places where the highest of concentrations of air pollutants was expected. Table 2 shows the conditions of taking of samples of air at workplaces.

Table 2. Air sampling conditions

Sorbents	**Air flow** [dm^3/h]	**Sample volume** [dm^3]	**Solvent**
Charcoal	20	100	Carbon disulphide
Glass fibre filter connected with tube included amberlite XAD-2 resin	120	600	Methanol
Silica gel	20	100	Acetonitrile, methanol
Silica gel coated ascorbic acid – gel „C”	30	150	Dichloromethane

Samples were analysed by a chromatographic method with the application of the following analytic arrangements:

a) a gas chromatograph HP - 6890 equipped with a “split-splitless” inlet working in the splitless system, a capillary column HP-5MS (30 m × 0.32 mm × 0.25 μm), a mass spectrometer HP 5972A and a computer with mass spectrum library. The walls of column were coated with the liquid phase (5 %-phenylene-95 %-dimethylsiloxane copolymer). Helium like carried gas flowed through the column in the amount of 1.8 cm^3 /min. The column worked in a programmable temperature.

b) a gas chromatograph Perkin Elmer AutoSystem GC 1022 equipped with a “split-splitless” inlet working in the split system (50:1), a capillary column PE -1 (60 m × 0.32 mm × 1 μm), a flame photometric detector (FPD) and a computer with Turbochrom programme. The walls

of column were coated with dimethylsiloxane. Helium like carried gas flowed through the column in the amount of 1.8 cm^3/min. The column worked in conditions a programmable temperature.

c) a gas chromatograph HP - 5890 equipped with a "split-splitless" inlet working in the splitless system, a capillary column HP-INNOWax (30 m × 0.25 mm × 0.25 μm), a alkcali flame ionization detector and HP 3396A as an electronic integrator. The walls of column were coated with bondable polyethylene glycol. Helium like carried gas flowed through the column in the amount of 1.2 cm^3 /min. The column worked in a programmable temperature.
d) a liquid chromatograph Gynkotek equipped with an autosampler, a column Nucleosil 100-C_{18}, a UV spectrophotometer detector and a computer.

Results of tests

The tests with use of the GC/MSD method showed the presence since a few to a dozen or so chemical substances in the analysed samples of air. Aliphatic compounds including to 30 carbons predominated among the identified chemical compounds.

As an example, the identified air pollutants in a rolling mill operator workstation air are shown in Table 3.

Table 3. Identified chemical substances present in a rolling mill operator workstation air

Compound name	CAS number	Retention time	Area %	MAC (mg m^{-3})
4-methyl-2-ethyl-1-penthanol	106-67-2	6,71	1,21	-
2,4-dimethylhexane	589-43-5	6,91	2,72	-
2,3,4-trimethylhexane	921-47-1	6,97	0,75	-
toluene	108-88-3	7,21	1,86	100
2-methylheptane	592-27-8	7,30	5,31	-
3-methlheptane	589-81-1	7,40	5,41	-
octane	111-65-9	7,83	5,41	1000
2,3,5-trimethylhexane	1069-53-0	8,09	0,13	-
2,5-dimethylheptane	2216-30-0	8,29	0,93	-
m-xylene	108-38-3	8,74	2,69	100
styrene	100-42-5	9,04	29,82	50
p-xylene	106-42-3	9,10	0,67	100
cumene	98-82-8	9,62	0,39	100

1-ethyl-2-methylbenzene	611-14-3	10,16	5,01	-
1,3,5-trimethylbenzene	108-67-8	10,42	0,32	100
3-cyclohexyl-1-carbonitrile	100-45-8	10,74	0,65	-
1,2,4-trimethylbenzene	95-63-6	10,87	0,77	100
benzothiazole	95-16-9	16,28	0,16	-
cyclohexyl isothiocyanate	1122-82-3	16,50	6,07	-
1,2-hydro-2,2,4-quinoline	147-47-7	30,24	0,16	-
benzothriazole	95-14-7	33,20	5,98	-
1-tertbutyl-4-methyl-5-nitrobenzene	72900-75-5	49,25	0,91	-
2,2-ditio(bis)benzothiazole	120-78-5	49,27	6,27	-
N-ethyl-1,3-ditioisoindoline	35373-06-9	53,37	0,91	-

The tests made it possible to identify a dozen or so organic compounds containing sulphur and nitrogen. The identified compounds at workstations with mixers, roll mills, calenders, and vulcanizing presses are shown in Table 4.

Table 4. Identified sulphur and nitrogen organic compounds in workplace air during the production of rubber plates and forwarding belts.

Workplace	Compound name
Mixer and rolling mill operator	**acetamide** **benzothiazole** **3-cyclohexyl-1-carbonitrile** **cyclohexyl isotiocyanate** N-ethyl-1,3-dithioisoindoline 1,4-dicyclopropancarbonitrile **2-imidazolidinethione** 2,2-ditio(bis)benzothiazole **N-nitrosodimethylamine** 2-mercapto-N-methylacetamide dimethylbenzylammonium chloride
Calender operator	**acetamide** **benzothiazole** **carbon disulphide,** **3-cyclohexyl-1-carbonitrile** **cyclohexyl isotiocyanate** N-ethyl-1,3-ditioisoindoline **2-imidazolidinethione** 2-methylbutylnitrile 2,3,5-trimethylpyridine
Vulcanizing press operator	**acetamide** **benzothiazole** **carbon disulphide** **3-cyclohexyl-1-carbonitrile** **cyclohexyl isotiocyanate** 1,2-dihydro-2,2,4-trimethylquinoline dimethylbenzylammonium chloride N-ethylbenzamine N-ethyl-1,3-ditioisoindoline **2-imidazolidinethione** 2-methylbutylnitrile

	2-mercapto-N-methylacetamide **N-nitrosodimethylamine** N-nitrosodipropyloamine N-nitrosopyrolidine 1-tertbutyl-4-methyl-5-nitrobenzene 5,6,7,8-tetrahydro-2-naphthylamine 2,4,6-trimethyl-1,4-dihydropyridine

Six of the identified chemical compounds of sulphur and nitrogen (printed in bold in Table 5) were identified at workstations air during the production of conveyer belts and rubber plates. These were: acetamide, benzothiazole, carbon disulphide, 3-cyclohexyl-1-carbonitrile, cyclohexyl isotiocyanate, 2-imidazolidinethione and N-nitrosodimethylamine.

The tests did not show the presence of highly toxic sulphur and nitrogen compounds like mercaptans, thiurams and carbamates in air at workstations of rubber compounds processing. The majority of the identified compounds are little / not well examined with regard to their influence on man and environment.

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