TECHNICAL
REPORT

ISO/TR
21275

First edition
2017-02

Rubber — Comprehensive review of the composition and nature of process fumes in the rubber industry

Caoutchouc — Examen exhaustif de la composition et de la nature des fumées de process dans l'industrie du caoutchouc

Reference number
ISO/TR 21275:2017(E)

ISO copyright office
Ch. de Blandonnet 8 • CP 401
CH-1214 Vernier, Geneva, Switzerland
Tel. +41 22 749 01 11
Fax +41 22 749 09 47
copyright@iso.org
www.iso.org

Contents

Page

Foreword

ISO (the International Organization for Standardization) is a worldwide federation of national standards bodies (ISO member bodies). The work of preparing International Standards is normally carried out through ISO technical committees. Each member body interested in a subject for which a technical committee has been established has the right to be represented on that committee. International organizations, governmental and non-governmental, in liaison with ISO, also take part in the work. ISO collaborates closely with the International Electrotechnical Commission (IEC) on all matters of electrotechnical standardization.

The procedures used to develop this document and those intended for its further maintenance are described in the ISO/IEC Directives, Part 1. In particular, the different approval criteria needed for the different types of ISO documents should be noted. This document was drafted in accordance with the editorial rules of the ISO/IEC Directives, Part 2 (see www.iso.org/directives).

Attention is drawn to the possibility that some of the elements of this document may be the subject of patent rights. ISO shall not be held responsible for identifying any or all such patent rights. Details of any patent rights identified during the development of the document will be in the Introduction and/or on the ISO list of patent declarations received (see www.iso.org/patents).

Any trade name used in this document is information given for the convenience of users and does not constitute an endorsement.

For an explanation on the meaning of ISO specific terms and expressions related to conformity assessment, as well as information about ISO's adherence to the World Trade Organization (WTO) principles in the Technical Barriers to Trade (TBT) see the following URL: www.iso.org/iso/foreword.html.

This document was prepared by Technical Committee ISO/TC 45, *Rubber and rubber products*.

Introduction

Fumes emitted during the rubber manufacturing processes were the topic of many studies. This comprehensive study was undertaken to compile and review published data with respect to rubber fume emissions in the workplace. This review has provided a comprehensive bank of technical data for dissemination and further debate. It has assessed literature regarding the chemical composition of rubber fumes in manufacturing from a comprehensive range of processes. It has been postulated that fume emissions from rubber compound vulcanization can be considered a single chemical entity, cited as posing a carcinogenic risk to human health. Although many studies have tried to characterize rubber fume emissions, there is no known concise study that provides a rational explanation for this conclusion. This study has tested this postulation and provided an insight as to whether it is a sound conclusion.

The aim of this project was to evaluate, on a basis of sound scientific literature, whether it is scientifically robust to consider “rubber fumes” as a homogeneous entity from a chemical point of view and, more importantly, in relation to measurement and control of occupational exposure risk for the rubber industry as a whole.

An extensive literature review aimed at providing a compilation of literature related to rubber fume emissions, this study has concentrated on the chemical compositional aspects of rubber fumes only and not on the toxicological or epidemiological aspects.

In addition, although rubber dust and rubber fumes are being considered by the EU for a potential incorporation in the scope of the Carcinogens Directive, this study has only considered rubber fumes.

This document provides detailed information on the study carried out, the results obtained from the literature reviews and the conclusions drawn from this information.

This document comprises two main parts; the first provides a general overview of the key areas of rubber technology and the second provides an extensive review of in-house and external literature on the composition and nature of rubber process fumes.

Natural rubber (NR) has been known to the civilized world since about 1493 when early European explorers found natives of Haiti playing with balls made from the exudates of a tree called “cau-uchu”. The term “rubber” was coined much later by the English chemist J.B. Priestly for its ability to erase lead pencil marks. The French scientist De La Condamine first introduced NR to Europe in 1736 and published his observations on the material in 1745. Industrial application of rubber only occurred after Charles Goodyear in 1841 discovered the process termed “vulcanization”, which converted the rubber to a more stable and useful material, that paved the way for the growth of the modern industry.

Synthetic rubbers were first produced in Germany in the 1930s, and during the Second World War when the supply of natural rubber was interrupted, methods were developed for the bulk production of synthetic rubbers. Styrene butadiene rubber (SBR) was one of the first synthetic rubbers to be developed and manufactured in high volume in the 1940s, mainly for the production of tyres and in an attempt to match the properties of natural rubber. Since that time, many different synthetic rubbers have been developed to allow the use of rubber in a very wide variety of environments and applications.

Over the years, the importance of rubber to modern life has constantly increased. This is not always immediately apparent because rubber components are often not colourful, eye catching or are used in applications where they are not readily visible. Natural and synthetic rubber compounds are used in a highly diverse range of rubber products which are manufactured throughout the world for various sectors of industry and for a variety of end users, including, but not exclusively, automotive, aerospace, medical/pharmaceutical, defence, commercial, general industrial and others.

Of the sectors where rubber is used, the automotive industry is of particular importance since tyre and tyre products account for approximately 60 % of the synthetic rubber and ~75 % of the natural rubber used today.

Table 1 provides an overview of the diverse range of rubber components made from general manufacturing processes and dipped latex technology. The list of components is by no means exhaustive but helps highlight the diverse areas and products in which rubber is used.

Table 1 — Range of rubber components

Tyres	passenger cars, trucks, racing vehicles, cycles, off-road tyres, inner tubes, curing bladders
Conveyor/ Transmission belting	steel cord conveyor belting, repair material for conveyor belting, scrapers, mining conveyors, V-belts, flat belts, synchronous belts
Industrial hoses	water hoses, high-pressure hoses, welding hoses, hydraulic hoses, spiral hoses, offshore hoses, oil hoses, chemical hoses
Automotive products	coolant hoses, fuel hoses, seals and gaskets, anti-vibration mounts, hydraulic hoses, fuel injectors, timing belts, window and door channelling, transmission and engine components, wiper blades, exhaust hangers
General mouldings/ Sheeting	moulded seals and gaskets, anti-vibration products, floor coverings, sheeting, tube rings, roofing layers, subsoil water sheeting, roller coverings, protection linings, moulded micro-cellular products, composite profiles, rubberized fabric, micro-cellular rubbers/profiles, wire and cable jackets and insulations, glass sealants, pump impellors, roof membranes, pond liners, rail mounts, bridge bearings, military vehicle track pads
Medical/ Pharmaceutical products	surgical gloves, medical tubing, MDI valve gaskets, catheters, dialysis products, surgical implants, prostheses, contraceptives, soothers, baby feeding teats and breast caps, blood transfusion tubing and valves, medical and antistatic sheeting and membranes, masks and respirators
Clothing	boots/footwear, protective suits, household gloves, industrial gloves, footwear/ boot heels and soling, cellular rubber soles, wet suits, diving suits, coated fabrics, sports footwear and clothing
Food contact products	food transportation (e.g. conveyer belts, hoses and tubing), food handling (gloves), pipe and machinery components (seals, gaskets, flexible connectors and diaphragm/butterfly valves), pumping system components (progressive cavity pumps stators, diaphragm pumps), plate heat exchanger gaskets, seals/gaskets for cans, bottles and closures
Potable water products	pipe seals and gaskets, hoses, linings of pumps and valves, tap washers, membranes in pipes and filters, coatings on process plant, tank linings
Miscellaneous products	adhesives, rubberized asphalt, high vacuum and radiation components, carpet backing, latex thread, sealants and caulking, toys

It is important that the reader of this document concludes that the rubber material used to make any particular product is not a single entity but is a complex compounded material referred to as a “compound” or “formulation”, which may contain a large number of essential chemical ingredients. These ingredients will include the base rubber polymer(s), reinforcing and non-reinforcing particulate fillers, process oils, vulcanizing agents, protective agents, process aids, etc. (all of which are available in many types and grades from many suppliers and can be included at different levels). The company or individual who designs a rubber formulation for a specific product has a vast number of ingredients to choose from and as such, many formulations are therefore possible for a specific rubber product.

The processing route by which the majority of rubber components are manufactured includes mixing the ingredients together in a controlled manner to produce a rubber “compound” or “mix”, shaping of the mixed compound to give the desired shape or form, then “vulcanizing” (also known as “crosslinking” and “curing”) the compound to convert it to a condition where it has permanent properties and shape.

The type of rubber materials and manufacturing processes used will depend upon the individual product and are described in this document. Many of the manufacturing processes involve generating heat in the rubber compound where volatile species such as “fumes” can be released from it.

The large diversity in both the rubber formulations available and the manufacturing processes used can therefore potentially give rise to a highly diverse range of species evolved.

In order to assist the reader to understand the terminology associated with the rubber technology in this document, a glossary of terms is included in Annex A.

Rubber — Comprehensive review of the composition and nature of process fumes in the rubber industry

1 Scope

This document, based on 95 publications, gives an overview of what is the composition of the fumes emitted during the rubber manufacturing processes. The results obtained confirm that rubber fumes are a complex and variable mix of chemicals which have a wide range of possible sources and origins, including chemicals generated from the chemical reactions occurring in the rubber compounds during processing and curing. Some of these chemical substances can be hazardous, others are not. This document demonstrates the need for International Standards to qualify and quantify the hazardous chemicals to which the operators in the factories producing rubber articles can be exposed to, allowing the identification and mitigation of potential health risks.

2 Normative references

There are no normative references in this document.

3 Terms and definitions

For the purposes of this document, the following terms and definitions apply.

ISO and IEC maintain terminological databases for use in standardization at the following addresses:

- IEC Electropedia: available at http://www.electropedia.org/
- ISO Online browsing platform: available at http://www.iso.org/obp

3.1
accelerator
compounding ingredient used in small amounts with a vulcanizing agent to increase the speed of vulcanization and/or enhance the physical properties of the vulcanizate

[SOURCE: ISO 1382:2012, 2.5]

3.2
activator
compounding ingredient used in small proportions to increase the effectiveness of an accelerator

[SOURCE: ISO 1382:2012, 2.6]

3.3
ageing
<act of> exposure of a material to an environment for a period of time

[SOURCE: ISO 1382:2012, 2.13]

3.4
ageing
<effect of> irreversible change of material properties during exposure to an environment for a period of time

[SOURCE: ISO 1382:2012, 2.14]

3.5
antidegradant
compounding ingredient used to retard deterioration by ageing

Note 1 to entry: Antidegradant is a generic term for certain additives such as antioxidants, antiozonants, waxes and other protective materials.

[SOURCE: ISO 1382:2012, 2.21]

3.6
antioxidant
compounding ingredient used to retard deterioration caused by oxidation

[SOURCE: ISO 1382:2012, 2.24]

3.7
autoclave
pressurized vessel used for vulcanizing rubber in a vapour or gas

[SOURCE: ISO 1382:2012, 2.33]

3.8
benzene
$C_6 H_6$
simplest member of the aromatic series of hydrocarbons

Note 1 to entry: It is colourless liquid with a b.p. of 80 °C and is used in the manufacture of many organic compounds.

3.9
blank
piece of rubber compound of suitable shape and volume to fill the mould

[SOURCE: ISO 1382:2012, 2.44]

3.10
bonding agent
substance, usually in liquid form, coated onto another material and used to produce a good bond between the material and rubber

[SOURCE: ISO 1382:2012, 2.54, modified — Note 1 to entry has been deleted.]

3.11
butadiene
$CH_2CHCHCH_2$
buta-1,3-diene
gas used in the manufacture of polybutadiene rubber and as one of the copolymers in the manufacture of styrene-butadiene and nitrile rubbers

3.12
calender
machine with two or more essentially parallel rolls, operating at selected surface speeds, nips and temperatures, for such operations as sheeting, laminating, skim coating (topping) and friction coating of a product to a controlled thickness and/or controlled surface characteristics

[SOURCE: ISO 1382:2012, 2.65]

3.13
carbon black
compounding ingredient consisting essentially of more than 95 % elemental carbon in the form of near-spherical particles with major diameters less than 1 µm, generally coalesced into aggregates

Note 1 to entry: Carbon black is produced by incomplete burning or thermal decomposition of hydrocarbons.

[SOURCE: ISO 1382:2012, 2.66]

3.14
chlorohydrin rubbers
class of synthetic elastomers based on epichlorohydrin

3.15
chloroprene rubber
CR
elastomeric materials composed of chloroprene

Note 1 to entry: It has fair to good resistance to petroleum-based fluids and good resistance to ozone and weathering.

[SOURCE: ISO 5598:2008, 3.2.96]

3.16
chlorosulfonated polyethylene
CSPE
elastomer made by substituting chlorine and sulfonyl chloride groups into polyethylene

Note 1 to entry: The material is best known by the trade name Hypalon (DuPont).

3.17
compound
intimate mixture of a rubber or rubbers or other polymer-forming materials with all the ingredients necessary for the finished product

Note 1 to entry: The term rubber is sometimes used to mean compound, but this use is deprecated.

[SOURCE: ISO 1382:2012, 2.96]

3.18
compounding
development of rubber compounds which will effectively withstand the conditions under which the products made from them are to be used

Note 1 to entry: The mixes so developed must be capable of being processed in the factory without undue difficulty.

Note 2 to entry: The term is also applied to the assembling of elastomer and compounding ingredients ready for mixing.

3.19
compounding ingredient
substance added to a rubber or rubber latex to form a mix

[SOURCE: ISO 1382:2012, 2.97]

3.20
compression moulding
moulding process in which the blank is placed directly in the mould cavity and compressed to shape by closure of the mould

[SOURCE: ISO 1382:2012, 2.98]

3.21
conveyor belting
belting used mainly in the transmission of materials, although increasing use is being made of conveyor belting in the transportation of passengers

3.22
crosslinking
<act of> insertion of crosslinks between or within rubber chains to give a network structure

[SOURCE: ISO 1382:2012, 2.118]

3.23
curing
application of accelerators and temperature for the establishment of chemical crosslinks between macromolecules of rubber

Note 1 to entry: This term is synonymous with vulcanization only in case of mixes containing sulfur. Some other chemicals are also used to establish these crosslink, for example, peroxide.

Note 2 to entry: The word curing is generally paired with a specific method, e.g. press curing, open steam curing, cold curing.

3.24
dispersion
<act of> distribution of one or more ingredients into a rubber, a rubber blend or a continuum material, by the application of shearing forces, in order to confer optimum and uniform properties

[SOURCE: ISO 1382:2012, 2.147]

3.25
double bond
bivalent gap
ethylenic linkage
bond in which two valency bonds link two atoms in a molecule

Note 1 to entry: It is typical of compounds showing unsaturation, such as ethylene. A double bond does not indicate extra strength of the bond but rather chemical instability and reactivity.

3.26
elastomer
macromolecular material which returns rapidly to approximately its initial dimensions and shape after substantial deformation by a weak stress and release of the stress

[SOURCE: ISO 1382:2012, 2.161]

3.27
extender
organic material used as a replacement for a portion of the rubber required in a compound

[SOURCE: ISO 1382:2012, 2.171]

3.28
extruder
machine which, through the use of a screw or a hydraulic ram, continuously shapes a material by forcing it through a die or dies

[SOURCE: ISO 1382:2012, 2.176]

3.29
filler
solid compounding ingredient, in particulate form, which may be added in relatively large proportions to a rubber or rubber latex for technical or economic purposes

[SOURCE: ISO 1382:2012, 2.184]

3.30
injection moulding
moulding process in which a rubber compound is forced into a closed mould from a separate chamber, by a pressure which is independent of the mould clamping force

[SOURCE: ISO 1382:2012, 2.242]

3.31
internal mixer
machine with temperature controls containing one or more rotors operating in a closed cavity used to masticate and/or to incorporate and disperse compounding ingredients into the rubber

[SOURCE: ISO 1382:2012, 2.242]

3.32
isoprene
2-methyl-1,3-butadiene
$CH_2C(CH_3)CHCH_2$
liquid hydrocarbon with boiling point 34°C

Note 1 to entry: It is regarded as the unit molecule of natural rubber, which is *polyisoprene* (3.43). Synthetic polyisoprene is marketed under a variety of trade names.

3.33
latex
colloidal aqueous dispersion of a polymeric material

[SOURCE: ISO 1382:2012, 2.250]

3.34
mill
two-roll mill
machine with two counter-rotating rolls, frequently heated or cooled, usually driven at different speeds, and having an adjustable nip for mastication, mixing, blending, warm-up or sheeting

[SOURCE: ISO 1382:2012, 2.274]

3.35
mix
mixture of rubber in any form with other compounding ingredients

Note 1 to entry: The term can apply to an incomplete rubber compound.

[SOURCE: ISO 1382:2012, 2.278]

3.36
mixer
machine which, through the action of mechanical work (shear), incorporates and disperses compounding ingredients into rubber(s) to form a mix or compound

[SOURCE: ISO 1382:2012, 2.279]

3.37
moulding
<process> process of shaping a material in a mould by applying pressure and, usually, heat

[SOURCE: ISO 1382:2012, 2.288]

3.38
natural rubber
cis-1,4-polyisoprene obtained from the botanical source *Hevea brasiliensis*

[SOURCE: ISO 1382:2012, 2.295]

3.39
nitrile rubber
elastomer resulting from the copolymerization of butadiene and acrylonitrile

3.40
oil resistance
resistance of an elastomer to swelling and ultimate degradation due to contact with or immersion in an oil

3.41
open mill
mill in which the rolls are exposed, in contrast to those of an internal mixer

3.42
plasticizer
compounding ingredient used to enhance the flexibility of a rubber or product, especially at low temperature

[SOURCE: ISO 1382:2012, 2.333]

3.43
polyisoprene
polymerized isoprene

Note 1 to entry: Naturally occurring polyisoprene are natural rubber (*cis*-form) and gutta percha (*trans*-form).

Note 2 to entry: The use of stereospecific catalysts has made possible the manufacture of synthetic *cis*-polyisoprene and *trans*-polyisoprene both of which are available commercially.

3.44
polymer
substance composed of molecules characterized by the multiple repetition of one or more species of atoms or groups of atoms (constitutional units) linked to each other in amounts sufficient to provide a set of properties that do not vary markedly with the addition or removal of one or a few of the constitutional units

[SOURCE: ISO 1382:2012, 2.341]

3.45
processing
variety of operations required to convert a raw elastomer into finished products

Note 1 to entry: Processing include calendering, *compounding* (3.18), *curing* (3.23), extrusion, mastication, mixing, spreading.

3.46
resin cure
vulcanization of elastomers effected by the incorporation in the compound of certain polymeric resins derived from the condensation of formaldehyde with 4-alkyl phenols

Note 1 to entry: Most frequently used with butyl and EPDM compounds for enhanced heat resistance.

3.47
retarder
compounding ingredient used to reduce the tendency of a rubber compound to vulcanize prematurely

[SOURCE: ISO 1382:2012, 2.383]

3.48
rubber
<products> family of polymeric materials which are flexible and elastic

Note 1 to entry: Rubber can be substantially deformed under stress, but recovers quickly to near its original shape when the stress is removed. It is usually made from a mixture of materials (solid or liquid), and in most products the base polymer is crosslinked by either chemical or physical links.

[SOURCE: ISO 1382:2012, 2.394]

3.49
rubber
<raw material> natural or synthetic elastic polymer (elastomer) which forms the basis of the compound used in many rubber products

[SOURCE: ISO 1382:2012, 2.395]

3.50
rubber
<rubber goods manufacturing> synonym for *compound* (the preferred term)

[SOURCE: ISO 1382:2012, 2.396]

3.51
silicone rubber
polyorganosiloxane, having a backbone structure consisting of alternating silicone and oxygen atoms with organic groups, usually methyl, vinyl or phenyl radicals, attached to the silicone member

Note 1 to entry: It is an elastomer of the silicone family.

3.52
unsaturation
<organic compounds> linking of some of the atoms of the molecule by more than one valency bond i.e., double or triple bonds

3.53
vulcanization
cure
process, usually involving heat, in which rubber, through a change in its chemical structure (for example, crosslinking), is converted to a condition in which the elastic properties are conferred or re-established or improved or extended over a greater range of temperatures

Note 1 to entry: In some cases, the process is carried to a point where the substance becomes rigid, e.g. ebonite.

[SOURCE: ISO 1382:2012, 2.513]

3.54
vulcanizing agent
curative
curing agent
compounding ingredient that produces crosslinking in rubber

[SOURCE: ISO 1382:2012, 2.515]

3.55
zinc oxide
activator in rubber compounds containing organic accelerators

4 Overview of the rubber industry

4.1 General

This clause is intended to give the reader a brief overview of rubber technology in order to provide some essential background information that will support and inform non-technical readers of the literature review. The overview is broken down into four specific areas (see 4.2 to 4.5) as detailed below, and encompasses the full spectrum of the rubber industry, with the fifth part (see 4.6) covering the effect of elevated temperature on the base polymers and rubber additives.

- Rubber component production processes
- Generic rubber types
- Rubber chemicals and additives
- Mechanistic chemistry of rubber vulcanization
- Effect of elevated temperature on rubbery polymers and rubber additives

4.2 Rubber component production processes

The wide diversity of rubber components in the market is highlighted in the Introduction. The rubber product manufacturing industry can be divided into four groups: 1) vehicle tyres, 2) engineering and industrial products, 3) latex products and 4) other miscellaneous rubber products.

The manufacturing processes involved in these industries have many similarities but there are also many differences. The differences relate to the raw material (whether using NR or synthetic rubber), the types of chemical additives used in the rubber formulations and the type of curing methods employed.

The main processing stages for the majority of rubber components manufactured involve the following:

- Mixing: The first stage of the rubber manufacturing process involves the production of a rubber formulation, (also known as a “mix” or “compound”). Mixing is of crucial and fundamental importance to the rubber industry. The base rubbers have to be extended with a variety of essential ingredients including plasticizers, reinforced with particulate fillers and important additives such as accelerators, curatives and protective agents, which all need to be thoroughly dispersed and distributed before the resultant compound can be shaped and vulcanized to give an end product with adequate properties. All these cannot be achieved without effective mixing.

  Rubber formulations vary significantly in their composition depending upon the desired characteristics of the product. As many as 15 to 20 different ingredients may be used in a single compound depending upon the polymer type and application fumes.

  The mixing equipment used to produce the rubber compounds includes internal batch mixers, mixing mills, continuous internal mixers and mixing extruders. The appropriate compounding ingredients for the formulation are normally weighed out in a compounding area or “drug” room before being loaded into the mixer at predetermined stages. However, it is also a practice, especially in the tyre manufacturing industry, for ingredients to be supplied preweighed by the supplier and added directly into the mixer.

- Shaping operations: Involves processes to convert the mixed compound into a suitable form/shape for the next stage of the process (e.g. extrusion to form profile shapes, calendering to produce sheeted material, milling to form moulding blanks, hand building, etc.).This will also include the processes where other reinforcing materials, including steel wire/cord or textiles are combined with the uncured rubber compound before being built/assembled into the final product before vulcanization.

- Vulcanization: For the vast majority of rubber product applications (except solution and latex adhesives, putty-like products, chewing gum-based products and some forms of sheeting), it is necessary to convert rubbery molecules into a stable three dimensional network so that recovery after deformation is essentially complete. In layman's terms, the process converts the rubber compound into a material which has much more stable properties over its intended working temperature range.

  To achieve this, it is necessary to undertake an irreversible process of crosslinking the polymer chains, which is known as "vulcanization", "crosslinking" or "curing". In the majority of cases, this occurs by heating the rubber compound at an elevated temperature to accelerate the chemical reaction and by pressurization of the material to consolidate it.

  The actual crosslinking mechanisms will be discussed in a later clause.

  The specific process method by which the product is vulcanized will depend on a number of factors, which may include formulation of the compound, physical form of the product required, the presence of other materials such as textile and steel reinforcement, and the size of the product.

- Post vulcanization processes: Other processes which may take place after the vulcanization stage to achieve final form or properties (e.g. post-curing, ancillary processes).

A generalized flowchart for rubber product manufacturing is shown in Figure 1 to provide the reader with some general guidance on the typical processes involved from raw materials to final product and how they are linked together. It must be emphasized that the actual process route involved will depend upon the actual product being manufactured. Therefore, not all rubber products will require all of the process steps shown in Figure 1.

A number of the rubber manufacturing process steps involve the generation of heat or have heat applied to them and therefore have the propensity for the generation of rubber fumes or volatiles from the rubber compound being processed. The processes highlighted in red in Figure 1 indicate where rubber fumes will be mainly generated, while those shown in pink indicate where there is also potential for rubber fumes to be generated, depending upon the precise operating conditions of the process.

The following points should be taken into account when considering the processes used to manufacture rubber products.

a) The process routes and actual processing equipment employed for each product type will be specific to that product.

b) The material mixing, shaping and vulcanization processing conditions (including time and temperature, etc.) employed for a particular product are not standardized throughout the industry, but will depend on a number of factors including polymer type, formulation, process equipment type, age and controls, product size and shape.

c) The main manufacturing processes where fumes are likely to be generated include mixing, moulding, vulcanization and post curing. The processes where fumes may be generated, depending upon the rubber formulations and processing conditions, include calendering, blank preparation, extrusion and spreading.

d) Some manufacturing plants will manufacture single product types with very few different compound formulation types utilizing the same processing equipment.

e) Other manufacturing plants may produce a large range of different products, utilizing a diverse range of rubber compound types and formulations, which employ a range of processing routes pertinent to the product.

f) The more modern factories or plants situated in more developed countries may have more automation and a good level of ventilation for many of the rubber manufacturing processes which generate fumes and where there is less direct contact by the employees. In contrast, within some of the Eastern or less-developed countries, there will be significantly less automation combined with older processing equipment, poorer ventilation and more direct employee contact with the rubber compound as it passes through the process, all of which would have a direct influence on the levels and types of fumes present.

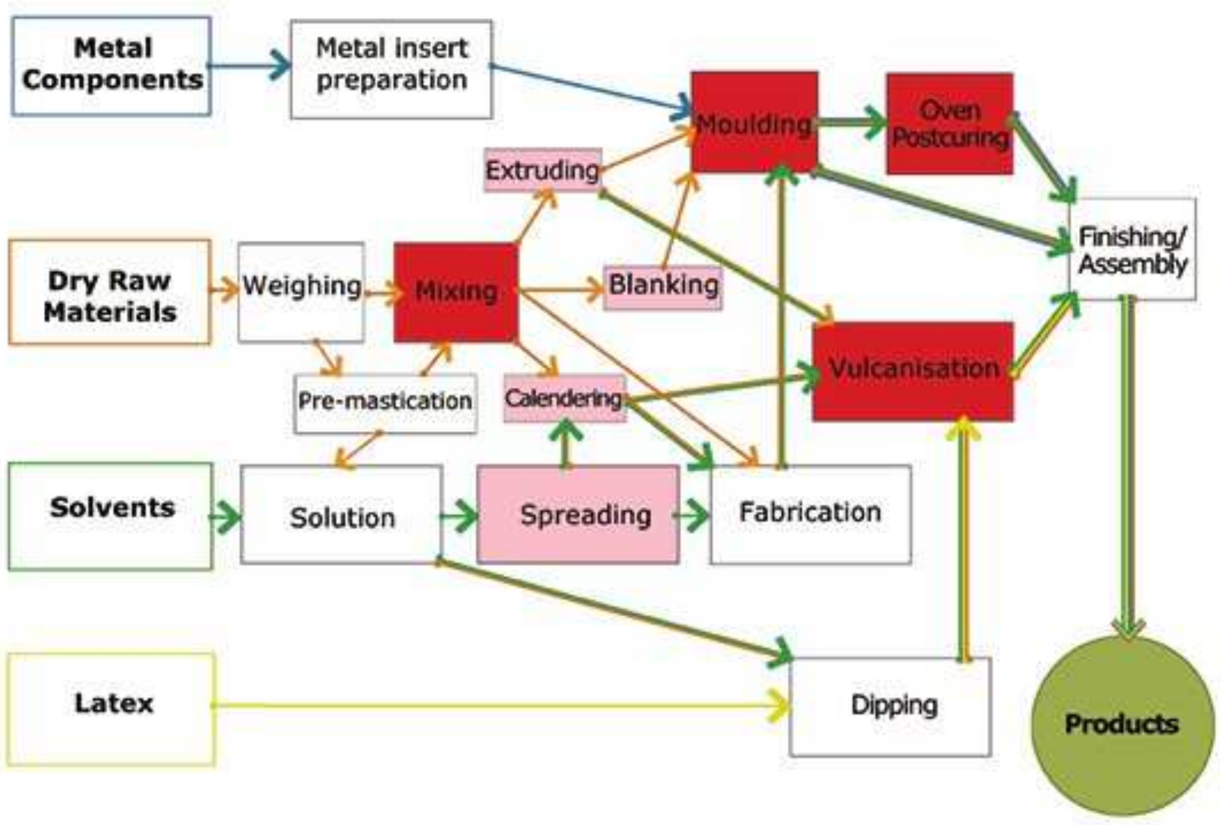
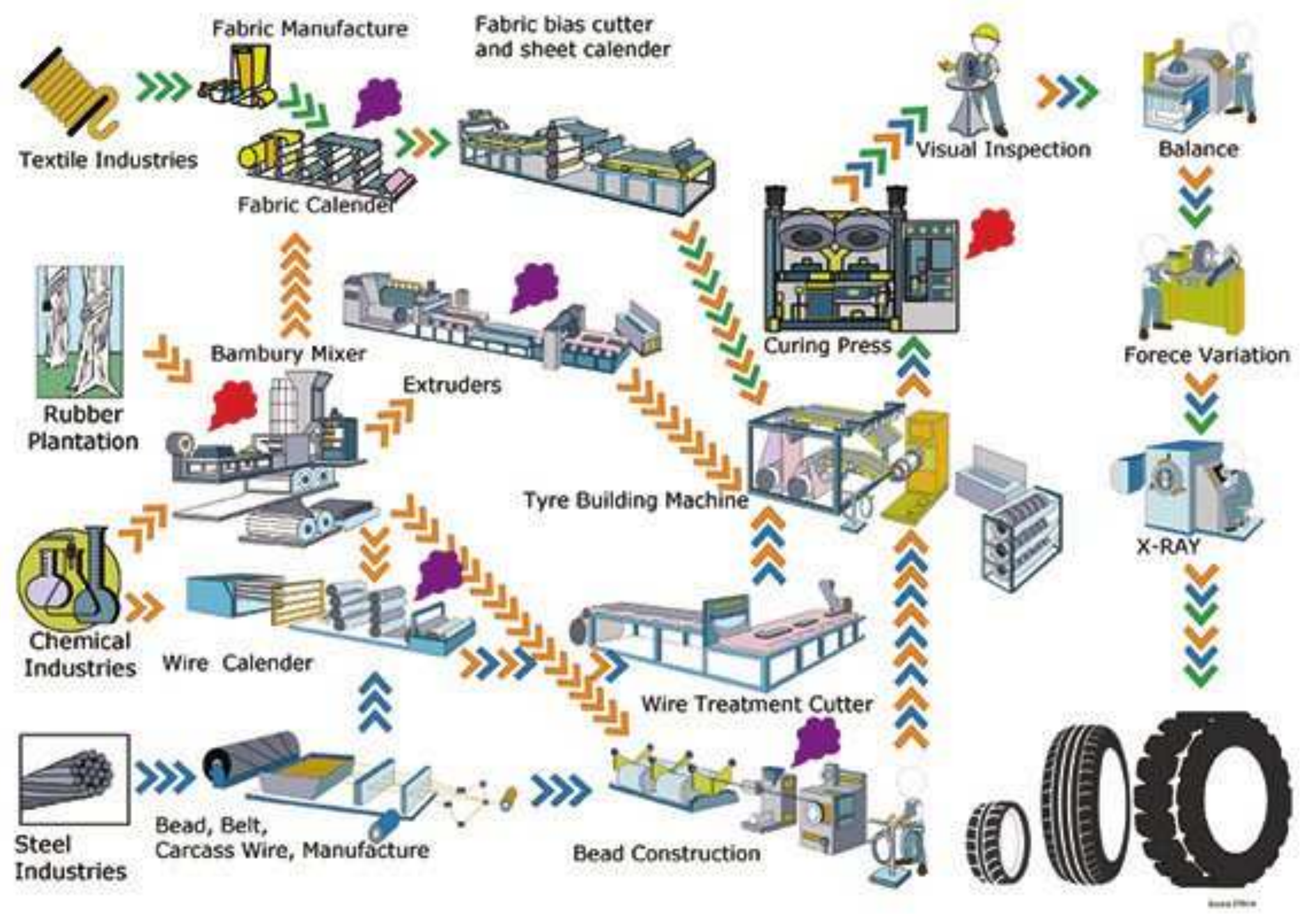


Figure 1 — Generalized flowchart for rubber product manufacture

A flowchart for the general processes involved in tyre manufacturing is shown in Figure 2. In a similar manner to Figure 1, the processes where rubber fumes will be generated are highlighted with the red symbol, 🟥, and those where there is also potential for rubber fumes to be generated depending upon the precise operating conditions of the process are highlighted with a purple symbol, 🟪.



Key

🟥 process where rubber fumes will be generated

🟪 process where fumes may be generated depending upon actual conditions

Figure 2 — Tyre manufacture flowchart

4.3 Generic rubber types

The following list identifies the main generic rubber types available in the market and gives their ISO designation in brackets. Each rubber has a unique chemical structure which has a direct influence on its inherent chemical and physical properties, processing behaviour and the applications and products in which it finds use.

- Natural rubber and natural rubber latex (NR)
- Polyisoprene (synthetic NR) (IR)
- Polybutadiene (BR)
- Styrene butadiene (SBR)
- Acrylonitrile butadiene rubber (also known as nitrile or NBR)
- Hydrogenated nitrile rubber (HNBR)
- Polychloroprene (CR)
- Butyl rubber (IIR) and halogenated butyl rubber (BIIR/CIIR)

- Ethylene propylene rubber (EP/EPDM)
- Epichlorohydrin rubbers (CO/ECO/ETER)
- Chlorinated polyethylene (CPE, CM)
- Chlorosulfonated polyethylene (CSM/CSPE)
- Polyacrylate rubbers (ACM)
- Ethylene-acrylic rubber (EACM, AEM)
- Ethylene-vinyl acetate (EVA, EAM)
- Silicone rubbers (MQ, VMQ, FVMQ, PVMQ)
- Fluorocarbon rubbers (FPM, FKM)
- Polyurethane (AU, EU, PU)
- Polysulfide rubber (OT, EOT)

The reader should take note that for each rubber type, there is a significant number of different grades available for selection from several polymer manufacturers, each of which may differ in the following aspects: supplier, polymer molecular weight and molecular weight distribution, polymerization type, polymerization stabilizer, co-monomer type and level, termonomer type and content, presence and level of pre-added carbon black filler, presence and level of pre-added process oil, etc. In the case of ethylene propylene polymers, for example, there are over 100 different grades available.

All rubber products are essentially made from compounded materials and each of the rubber types needs to be specifically formulated with a range of other essential additives to achieve a rubber "compound" that has the desired processing and properties related to the product manufactured.

It should also be noted that not only are rubbers used individually, but are often used in blends where two or even three rubber types are mixed and blended together, again in various ratios, in order to achieve the desired product performance and properties. Tyre component compounds are examples of this.

Taking all of the above aspects into consideration, it can be concluded that the large range of rubber grades available creates the possibility for the rubber compounder to design an infinite number of rubber formulations for any given product or application.

All of the factors mentioned above will influence the breakdown products produced when the rubber is processed.

The rubber compounder must determine which rubber type is appropriate for a given application and assist with that selection process. Consideration has to be given to factors such as temperature resistance and oil resistance of each rubber.

4.4 Rubber chemicals and additives

Rubber products are manufactured from "compounds" or "formulations" which can comprise a range of essential ingredients necessary to allow the material to be processed satisfactorily and achieve the properties required in service. When considering the manufacturing of rubber components, it must therefore be taken into account that they are "compounded" materials.

The principal classes of rubber compounding chemicals include the following:

- rubbers (see 4.3);
- vulcanization accelerators;
- activators, retarders and inhibitors;

- vulcanizing agents;
- antidegradants;
- fillers;
- plasticizers/softeners;
- process aids;
- miscellaneous additives.

Each of these classes of materials plays a vital role in the rubber compound, and within each class of ingredient, there is a wide range of different chemical compounds available on the market.

In considering the rubber chemicals used in the rubber industry, the following should be taken into account in relation to rubber fumes generation.

- Rubber products comprise materials which can contain a wide range of chemical additives.
- Although there are general guidelines for design of rubber compounds in regard to the ingredients used, the final formulation depends upon the knowledge of each rubber compounder. The highly diverse classes and ranges of ingredients available mean that there are no "standard" formulations for any one product or component; therefore, there are potentially an infinite number of rubber formulations on the market.
- Within each class of ingredients, there are numerous manufacturers offering a diverse range of additives, which are not chemically identical, adding to the range of rubber formulations possible.
- Depending on the rubber type and application, the number of ingredients used in a rubber compound can vary from 4 or 5 up to 15 to 20 different ingredients, with diene-based rubber containing the highest numbers of ingredients. Whereas, more specialized rubbers such as silicone and fluorocarbons contain the least.
- It is also common practice to use more than one ingredient from a particular class in a formulation to achieve the desired processing and final properties, which adds to the diversity of compounds available (e.g. two or more accelerators, antidegradants, carbon black fillers, black and mineral fillers, etc.).

4.5 Mechanistic chemistry of rubber vulcanization

4.5.1 Generality

The range of rubber polymers available, as well as the significant differences in their chemical structures is described in 4.3. As a result of these differences, not all of the rubber types can be crosslinked by a single type of cure system, and therefore, the system used to crosslink them will be directly related to the individual chemical structure of the rubber in question. The fact that the cure system chemistry is markedly different for each type will also mean that the breakdown products from compounds containing these different cure systems will also vary.

The crosslinking systems available are discussed in 4.5.2 to 4.5.5.

4.5.2 Sulfur-accelerated cure systems

A very large proportion of rubber products are based on compounds produced using unsaturated (diene) rubbers. Their chemical structures contain double bonds throughout the polymer chains that provide reactive sites through which the crosslinking reaction by formation of covalent bonds takes place. Due to the presence of these reactive sites, crosslinking using accelerated sulfur systems is possible and these systems dominate much of the market.

The chemistry of sulfur vulcanization is highly complex and even today, only the main stages are proven and there is still much to be understood about the effects of various cure system additives.

4.5.3 Peroxide-based cure systems

In terms of volume production, the number of rubber products containing peroxide-based curing systems is considerably lower than those containing sulfur-based systems.

The rubber types that contain no unsaturation in their polymer structure, known as saturated rubbers, cannot be crosslinked using sulfur and therefore, the only practical way of vulcanizing saturated rubber is by use of a free radical generating technique. There are a range of rubber types capable of being crosslinked with peroxides, which includes saturated and some unsaturated rubbers listed in Table 2.

Table 2 — Range of rubber types capable of being crosslinked with peroxides

Peroxide crosslinking possible for:					
NR	— Natural rubber	AU/EU	— Polyurethane rubber		
IR	— Polyisoprene rubber	EPM	— Ethylene propylene copolymer		
BR	— Polybutadiene rubber	EPDM	— Ethylene propylene terpolymer		
CR	— Polychloroprene rubber	T	— Polysulfide rubber		
SBR	— Styrene butadiene rubber	CSM	— Chlorosulfonyl polyethylene		
NBR	— Butadiene acrylonitrile rubber	—	— Ethylene acrylic rubber		
HNBR	— Hydrogenated butadiene acrylonitrile rubber	EBA	— Ethylene butyl acrylate		
Q	— Silicone rubber	FPM	— Fluoro rubber		
Peroxide crosslinking possible with blends of:					
NBR/EPDM		PE/EPDM		NBR/EVA	
SBR/EPDM		EPDM/PP			
Peroxide crosslinking limited or impossible for:					
ACM	— Polyacrylate rubber	CO	— Epichlorohydrin rubber	PB	— Polybutadiene-1
IIR	— Butyl rubber	ECO	— Epichlorohydrin copolymer	PIB	— Polyisobutene
CIIR	— Chlorobutyl rubber				

As with sulfur vulcanization, crosslinking using peroxides is also chemically very complex and has been studied by many workers over a number of years. Because of the variety of reactions, widely different behaviour is said to occur with different rubbers and different peroxides, while the presence of co-agents can have considerable influence. The breakdown products from these cure systems are therefore different from the other cure systems.

4.5.4 Metal oxides

The presence of halogens (chlorine, bromine or fluorine) along the polymer chain of unsaturated rubbers tend to “deactivate” the double bond, meaning that sulfur vulcanization is not possible and other cure system types are needed.

Cure systems based on zinc and magnesium oxides are therefore used to effectively crosslink polychloroprene rubber and chlorosulfonated polyethylene rubbers.

4.5.5 Other vulcanizing systems

There are several other vulcanization systems beyond the ones already described, which tend to be used to vulcanize some of the lower volume rubber types. These include polyfunctional amines which can be used to crosslink polychloroprene homopolymer, polyacrylate rubbers, epichlorohydrin rubbers and some fluorocarbon rubbers. In addition, quinone dioxime and phenolic resin cure systems are also used to vulcanize specific types of butyl rubber.

4.6 Effect of elevated temperature on rubbery polymers and rubber additives

Due to their chemical complexity, there are a large number of reactions and interactions that do occur, and have the potential to occur, when rubber compounds are subjected to high temperatures. These elevated temperatures affect a wide range of ingredients and components within rubber compounds, including:

a) base polymer and chemical species within rubber compounds such as polymerization aids and residual monomers;

b) reactive, functional additives such as antioxidants and other additives which are reactive and play a role in vulcanization, e.g. accelerators and co-agents;

c) low molecular weight additives and low molecular weight fractions within multi-component additives such as oils.

When a rubber is heated, there are several mechanisms and routes that generate low molecular weight compounds that have the potential to contribute to rubber fumes. Some of these involve degradation reactions and others involve such things as stabilization reactions and reactions associated with the vulcanization of the rubber.

5 Definition of rubber fumes

The definition of rubber fumes was established by ISO/TC 45 as "*a variety of substances emitted from rubber compounds into a workplace atmosphere as a result of industrial processing, the composition of which depends on the formulation of the compounds concerned, the process technology in use and the associated process parameters*."[94]

The above definition was based on the definition given by the UK Health and Safety Executive (HSE) in its EH40 publication and the Method for Determination of Hazardous Substance (MDHS) Number 47, which have been in use in the UK rubber industry for a number of years. The HSE definition is as follows.

"Rubber fumes are evolved in the mixing, milling and blending of natural rubber and rubber or synthetic elastomers, or of natural rubber and synthetic polymers combined with chemicals, and in the processes which convert the resultant blends into finished products or parts thereof, and including any inspection procedures where fumes continues to be evolved".

In addition to high-temperature vulcanization processes where chemical crosslinking reactions occurred and produced low molecular weight reaction by-products, the HSE definition also included operations that were conducted at lower temperatures, but which can result in the volatilization of constituents within the rubber.

The HSE definition addresses the various situations in which rubber fumes can be generated, but does not address its composition. Therefore, to provide a more complete definition of rubber fumes, this compositional element has also been taken into account. From consulting authoritative studies and information sources, it emerges that any consideration of the chemical nature and composition of rubber fumes should include the following classes of species:

a) gases, e.g. carbon disulfide;

b) vapours, e.g. volatile liquids such as toluene;

c) aerosols, e.g. hydrocarbon oil and plasticizers;

d) special case compounds, e.g. N-nitrosamines, aromatic amines and polyaromatic hydrocarbons (PAHs).

Considering all of these classes of compound ensures that a comprehensive evaluation of the composition and nature of rubber fumes is undertaken, with no species being overlooked or disregarded. In general, rubber fumes can be considered as being comprised of both "visible" and "invisible" fractions. The gases and vapours in the list above make up what can be regarded as the “invisible” component of rubber fumes, with the aerosols forming the “visible” component.

The 1974/75 BRMA/Rapra environmental survey reported that the solvent-soluble portion of airborne particulates provides an effective measure of “visible” fumes from hot rubber. The MDHS Method 47 for the determination of rubber fumes and rubber dust, which has already been referred to above, uses the cyclohexane-soluble fraction of the airborne contamination collected on a glass fibre filter as being the rubber fumes portion, with the insoluble fraction being regarded as the rubber dust fraction.

To obtain analytical data on the “invisible” (i.e. gases and vapours) fraction of rubber fumes, several approaches have been used by scientists over the years. A popular method involves trapping the compounds (ISO/TS 17796) and then using a chromatographic technique (e.g. GC-MS) to separate and identify the various compounds that have been trapped. In some cases, specialized equipment has been manufactured that closely mimics the curing processes used in the industry (e.g. compression moulding) and is interfaced with the analytical equipment in such a way that it transports the fumes directly into it, thus avoiding, as far as possible, any losses that may take place when an intermediate “trapping” stage is employed.

Finally, for the basis of this study, this multi-component (or class) definition of rubber fumes described in the above paragraphs is being used as a means of evaluating the existing literature and it is not necessarily being proposed as a future means for defining rubber fumes.

6 Nature and composition of rubber fumes

6.1 General

Based on the results of the literature search, this clause provides a summary of the nature and composition of rubber fumes with regard to the variety of chemical compounds that can be present, their origins, the different physical forms in which they can exist within the factory environment (i.e. gases, aerosols, etc.), and the challenges that have to be met in order to trap and analyse rubber fumes effectively. Further information on the references cited in this clause is provided in Clause 8.

As shown in 6.4, there have been many changes in rubber technology over the past 40 years in response to an increasing awareness in the need to protect the health of workers and these mean that the composition of rubber fumes has also changed over this period.

6.2 Key components of rubber fumes and their origin

The work that has been carried out to characterize rubber fumes has shown that it comprises a wide range of chemical species with respect to molecular weight and compound type (i.e. polarity and structure). Several studies have reported over 30 different species in the fumes from a particular rubber compound, and the extensive work carried out by Rapra Technology, and other organizations such as Trelleborg Industri AB, Aspen Research and the German Institute for Rubber Technology, have shown that over 150 different chemical species could be detected in the fumes generated by the vulcanization of 40 different compounds using a “pool” of 75 compounding ingredients.

With respect to the range of chemical species types present in rubber fumes, several scientists have identified that a large range of chemical species are present, with the following types being represented:

a) aliphatic hydrocarbons — straight chain and cyclic;

b) aromatic hydrocarbons;

c) halogenated compounds;

d) isothiocyanates;

e) ketones;

f) nitrosamines;

g) thiazoles;

h) aldehydes and alcohols;

i) esters and ethers;

j) amines and nitrosamines;

k) sulfur compounds.

The relative contribution of these to any given sample of rubber fumes are dependent on the ingredients present in each rubber compound contributing to the fumes present in the working atmosphere at a particular moment in time.

This wide range of species in rubber process fumes is present in many physical forms, e.g. gases, vapours and aerosols. The relative levels of these different physical forms vary according to the different areas (e.g. mixing, moulding, storage, etc.) within the rubber factory (see Clause 7). There are three distinct sources of volatile compounds that will be present in rubber fumes:

- volatile ingredients, e.g. antioxidants and plasticizers;
- volatile impurities in ingredients, e.g. residual monomers and manufacturing impurities;
- volatile reaction and breakdown products of chemical reactions that occur during processing, e.g. vulcanization and anti-oxidant activity.

6.3 Trapping and analysis of rubber fumes

6.3.1 General

Several methods and techniques have been used for the trapping and analysis of rubber fumes. Bearing the compositional complexity described in 6.1 in mind, these methods and techniques have been designed to achieve the most accurate characterization possible.

The work that has been carried out falls broadly into two different categories: that which has been done within factory environments and that which has been carried out under laboratory conditions. A summary of the work carried out in the two different areas is shown in the subsequent subclauses.

6.3.2 Characterization studies carried out in factory environments

The Health and Safety Executive published MDHS Method 47/2 for the determination of rubber dust and fumes in rubber factories in 1985 and published a revised version in 1999.[72] This is the standard method used in the UK and the methods used in several other countries are based on it. However, this method can encounter difficulties when it is used in situations where there is cyclohexane soluble organic dust, and cyclohexane soluble rubber chemicals, such as stearic acid, both resulting in an overestimation of the amount of rubber fumes present. Also, an analysis of the rubber dust and fumes data on the European Union Concerted Action programme database has shown that using polytetrafluoroethylene (PTFE) filters, rather than glass fibre filters recommended by MDHS 47/2, can influence the results obtained.

Another approach taken in response to the complexity of rubber fumes is to carry out mathematical modelling of the emissions, particularly to assist in the design of industrial equipment for the collection of fumes. An example where this has been used is to profile the emissions from the opening of compression moulds in the manufacture of tyres where one estimate puts the number of possible chemical compounds at up to 400. Once these models have been developed, experimental data has been obtained on the actual fumes to check on the accuracy of the predictions.

The visible fraction of rubber fumes, the aerosols fraction, is believed to be formed at two stages in the production process: the mixing stage (due to the large mechanical stresses and local overheating within the rubber compound) and the vulcanization stage (due to the condensation of vapours of high boiling point substances). In both cases, the aerosol particles contain numerous substances captured by the oil-like material forming the aerosol. Data which has been obtained on the aerosol that was associated with the vulcanization fumes from a particular nitrile rubber compound has shown it to be mainly comprised (90 %) of plasticizers within the compound.

In order to trap, identify and quantify as many components of rubber fumes as possible, it is necessary to design and use multifaceted sampling and analysis methodologies. Table 3 gives an example of such a system, which has been validated for a total of approximately 50 single chemical substances.[55][56]

Table 3 — Details of a multifaceted sampling and analysis system for rubber fumes

Substance	Collection media	Analysis method
Highly volatile aliphatic and aromatic compounds	Activated charcoal	GC or GC-MS
Amines and amides	Silica gel	GC-NPD
Highly volatile chlorinated compounds	Activated charcoal	GC-ECD
Carbon disulfide and highly volatile sulfur compounds	Sampling bag	GC-FPD
Aldehydes and ketones	Silica gel	HPLC-UV
Low volatility compounds	XAD-2 Adsorbent	GC or GC-MS
Aerosols	Glass fibre filter	FT-IR

ISO/TS 17796 specifies a qualitative method of TD-GC-MS for the identification of volatile components in rubber fumes, after trapping on a solid sorbent based on 2,6-diphenylphenylene oxide polymer resin. It is applicable to a screening of emissions from the processing of rubber compounds in the ambient workplace and storage environment. Its application enables specific compounds in rubber fumes to be identified and allows the potential to assess the contribution of certain compounding ingredients to the fumes. By identifying substances, it also provides characterization data that the HSE 47/2 method, being a solely cumulative quantitative method, does not. However, it has limitations, which includes the fact that it only identifies substances and does not quantify them and that the data obtained will be influenced by the inherent specificity of the sorbent used for the trapping stage. For example, the sorbent used in this method will not be capable of efficiently trapping and retaining all of the types of substances listed in Table 3. Data generated using this ISO method has been published[74] and is reproduced in 8.1.2.

6.3.3 Characterization studies carried out under laboratory conditions

In some cases, laboratory-based systems have been designed and assembled for the generation and characterization of rubber fumes. One of the most extensive examples of these was the programme of work carried out by Rapra Technology from the late 1970s until the late 1980s. In this work, a gas transfer mould which was capable of mimicking a compression moulding process was directly interfaced to a GC-MS. This ensured that representative fumes samples were generated and then transferred into the analytical instrument quickly and with negligible loss as no intermediate trapping stage (which can introduce biases) was involved. A large number of experiments using different rubber compounds were performed using this set up and the data obtained on the rubber fumes that was generated, with over 150 different species being identified, enabled a number of important ingredient/process condition relationships to be established.

A laboratory-based system for studying the composition of rubber fumes, similar to the one set up by Rapra Technology, was implemented by workers at Aspen Research. This consisted of a moulding press coupled to a GC-MS, and enabled a rapid screening of various rubber formulations for the identification and quantification of organic compounds present in their vulcanization fumes. The results reported were from nine different vulcanizates typically used in the industry (SBR-, NR-, NBR-, CR- and EPDM-based compounds). The effect of curing time and pressure were investigated, as well as recipe changes within a given compound series.

Other approaches to characterize rubber fumes in the laboratory have involved the generation of fumes by heated reactor cells, cure simulation apparatus that enables continuous sampling of the evolved fumes to take place, and headspace GC-MS techniques. These methods seek to analyse the fumes as directly as possible without the need to trap/collect it using an intermediate stage and have made valuable contributions to the understanding of its nature and complexity.

6.4 Changes in rubber technology that have influenced the nature and composition of rubber fumes and improved the protection of workers in the industry

6.4.1 General

There have been a number of changes in rubber technology over the years (e.g. the move to low or nitrosamine free accelerators, and the reduction in PAHs in process oils) that had an impact on the composition of rubber fumes and have resulted in improvements in the protection of workers in the rubber industry, reducing the level of exposure to rubber fumes in general.

Some of these changes have been brought in slowly over many years, and below is a brief summary of the main examples that have been revealed by the literature search, which is provided in full, with additional information on the references cited in Clause 8.

6.4.2 Overall trend in rubber workers' exposure to total rubber fumes

An analysis of the rubber dust and fumes data on the European Union Concerted Action programme database[19] has shown that the level of exposure to total rubber fumes has declined by around 4 % per year from the mid-1970s to 2003. This reduction is believed to be due to several factors, such as improvements in the design of ventilation and extraction systems, changes in working practices and changes in technology such as using intermixers instead of open-mill mixing.

6.4.3 Polyaromatic hydrocarbons

Polyaromatic hydrocarbons (PAHs) have been the focus of attention for many years, with scientists commenting on their presence in rubber products (due to the use of hydrocarbon process oils) and hence, rubber fumes in the 1970s. The situation remained reasonably constant until the late 1990s when environmental concerns associated with their presence in tyre rubber deposited on roads in Scandinavian countries, e.g. Sweden, led to the development of low-PAH content extender oils for use in tyres.

6.4.4 Nitrosamines

The presence of nitrosamines in rubber compounds and rubber fumes has also been recognized for many years. One of the main drivers that brought about a change in the rubber technology used in the EU was the issuing in the mid-1980s by German authorities of stringent new guidelines on N-nitrosamine content in factory atmospheres. To address these low limits, new accelerators for the curing of rubber were developed, which either have secondary amine breakdown products that are less likely to form nitrosamines or will not form any nitrosatable breakdown products at all.

6.4.5 Silane coupling agents and resorcinol steel cord coating agent

Two other examples, both in the tyre industry, where the influence of specific additives on the composition of rubber fumes has been addressed over the past 25 years are silane coupling agents (which liberate ethanol during use) and resorcinol steel cord bonding agent. In the first case, new low volatile content coupling agents have been developed and, in the case of resorcinol, the use of predispersed resorcinol to reduce fumes and odour has been investigated.

7 Factors affecting the variability of rubber fumes

7.1 General

As with Clause 6 which is based on the results of the literature search, this clause provides an overview of the principal factors that affect the variability of rubber fumes. Further information on the references cited in this clause is provided in Clause 8.

7.2 Influence of the rubber compound formulation on the composition of rubber fumes

Many workers have demonstrated that the chemical species that are in rubber fumes directly relate to the ingredients present in a rubber compound.

An example of the published data[30] that illustrates this is shown in Table 4. In this table, different compounds that are basic in character that have been detected in the fumes emitted from five different types of rubber are listed.

Table 4 — Basic compounds detected in the fumes from five different rubbers

Rubber type	Fraction of fumes	Compounds identified
SBR	Basic	Aniline, acridine or benzoquinoline, phthalimide, dicyclohexylamine, 2-(4-morpholinyl)benzothiazole, 6PPD
EPDM	Basic	Morpholine, N-cyclohexyl formamide, cyclohexylamine, N-butyl 1-butanamide, di-isobutyl phthalate, 2-cyclohexyl benzothiazole
NBR	Basic	Dimethyl-2-butanamine, 3-(diethylamino) propane nitrile, nicotine, tetrabutyl urea, phthalates, aniline,
Butyl	Basic	Benzidine, N-(2,2-dimethylpropyl)-N-methyl benzenamine, N-ethyl-2-benzothiazolamine, benzothiazole, phenyl benzimidazole
SBR/NR	Basic	N-cyclohexylmethanamide, cyclohexyl isothiocyanate, chloroalkanes, phthalates, aniline, nicotine

NOTE 1 The nicotine in the lists above could have been due to operatives smoking while the fumes were being collected.

NOTE 2 In some cases, species that would not be expected to be present in the rubber fumes of the particular compound being studied are reported (e.g. phthalate from an EPDM). This could be due to process fumes from other rubbers being processed nearby, e.g. a Nitrile rubber in the EPDM case.

NOTE 3 The terms “Fraction of fumes” and “Basic” relate to the fact that the fumes collected was separated into five separate fractions: basic, acidic, polar neutral, aliphatic and aromatic. Only the data obtained on the “Basic” fraction is shown in this table.

7.3 Influence of different manufacturing processes on rubber fumes

In addition to the composition of rubber, two other factors that have a large influence on rubber fumes are the particular manufacturing process (e.g. moulding, extruding, calendering, etc.) and the processing temperature, which will be discussed in this subclause and subsequent subclauses.

It has already been mentioned in 6.1 that the type of process employed in a rubber factory can affect the nature of rubber fumes, with aerosols mainly being formed in the mixing and vulcanization stages. In the case of the other fraction, the “invisible” (gases and vapours) fraction, although some are present in mixing fumes and in the stores where finished rubber products are kept, the greatest concentration is present in vulcanization fumes.

Taking into account total fumes (i.e. both visible and invisible fractions) within a particular rubber factory, the overall levels of fumes vary according to the type of process being carried out, i.e. mixing, extruding, moulding, storage, etc. For example, in the general rubber goods (GRG) sector, the overall level of exposure to rubber fumes has been found to vary as shown below:

Moulding > Extrusion > Milling

These differences relate to factors such as temperature and the amount of surface area exposed to the atmosphere.

An example of the fumes data that has been obtained on the volatile organic substances (VOS) in different areas of a tyre manufacturing site is shown in Table 5.[17]

Table 5 — Volatile organic substances detected in different areas of a tyre manufacturing site

Production area	Specific area	Number of identified VOS	Total content of VOS (mg/m^3)
Mixing department	Internal mixer	47	99,1
	Mill	37	17,7
	Ventilation	63	10,1
Vulcanization	Shaper-vulcanizer	55	21,7
Finished product storehouse	Working zone	55	31,1
	Ventilation	24	7,8
VOS = Volatile organic substances			

7.4 Influence of different processing temperatures on the composition of rubber fumes

Work carried out by Willoughby[1] using the Rapra GTM/GC-MS combination with an SBR compound, illustrated how the processing temperature can affect the types and levels of hydrocarbon species that are detectable in its fumes. This data is shown in Table 6.

Table 6 — Effect of vulcanization temperature on levels of particular hydrocarbon compounds in fumes from an SBR compound

Hydrocarbon compound in fumes	Extrusion (up to 110 °C) µg/m^3	Vulcanization 1 (at 145 °C to 165 °C) µg/m^3	Vulcanization 2 (at 180 °C to 240 °C) µg/m^3
Benzene	25–180	10–1 200	8–15
Toluene	20–160	6–800	4–8
Styrene	1–20	2–180	90–500
Ethylbenzene	1–15	2–90	30–150
4-Vinylcyclohexene	0–3	ND	30–210
Isopropylbenzene	0–10	2–200	60–250
Di-isopropylbenzene	0–7	1–75	35–70
Dodecenes	0–20	5–180	300–7 000
Cyclododecatriene	1–10	5–400	ND
D = Detected but not quantified ND = Not detected			

As shown in Table 6, the situation is complicated, with the levels of some compounds reducing and others increasing as the vulcanization temperature is increased.

Rapra also reported[2] on the effect that changing the moulding temperature has on the amount of a particular reaction product (in this case, carbon disulfide) released from a sulfur cured EPDM rubber containing the accelerator TMTD. Increasing the temperature in steps from 150 °C to 200 °C and finally 250 °C, increased the amount of carbon disulfide released from 1,03 m.mole, to 1,91 m.mole, and finally to 2,34 m.mol. This work by Rapra also demonstrated that by modifying the cure system, no carbon disulfide is liberated.

Another reported example[3] of the effect of process temperature involves the amount of TDI liberated from a urethane adduct curing agent for NR compounds. The amount of free TDI found in the vulcanization fumes was found to reduce as the temperature was reduced from 200 °C to 153 °C. Different levels of free TDI were also found for the same compound above a mixing mill and above a moulding press, showing the effect that different processes and processing conditions can have.

Finally, another Rapra paper[4] showed how the total amount of rubber fumes, determined as total weight loss, varies with vulcanization temperature. As expected, the total amount of fumes was found to increase as temperature rises, as shown below:

- at 160 °C, 0,18 %;
- at 175 °C, 0,5 %;
- at 190 °C, 0,75 %.

8 Review of literature on the composition and nature of rubber process fumes

8.1 Comprehensive literature search

8.1.1 General

In this subclause, the results that have been obtained on the composition and nature of rubber fumes by carrying out a comprehensive literature search are reported.

The majority of the articles are taken from journals chosen according to technical merit, subject matter (i.e. polymers and polymer related) and are peer reviewed.

8.1.2 Rubber fumes data obtained from factory atmospheres

Frolikova, et al.[17] reported where levels of various toxic substances in the air in different departments of a tyre factory were compared and toxic substance released from styrene-butadiene rubbers, polyisoprene, carbon black, vulcanizing agents and process oils were listed.

For example, some of the species found to be released from a butadiene-styrene polymer used in tyre manufacturing (SKMS-30ARK) and heated to 180 °C (a typical vulcanization temperature) were the following:

- styrene;
- toluene;
- ethyl benzene;
- 4-vinylcyclohexene;
- isododecene;
- alpha-methyl styrene.

In addition to working directly with tyre ingredients, monitoring work in various working areas within a tyre factory was undertaken to determine the number and total level of volatile organic substances (VOS) that were present. The results obtained show that VOS in different production areas differ considerably, as shown in Table 7.

Table 7 — Variation in levels of volatile organic substances found in different areas of a tyre factory

Production area	Specific area	Number of identified VOS	Total content of VOS (mg/m^3)
Mixing department	Internal mixer	47	99,1
	Mill	37	17,7
	Ventilation	63	10,1

Table 7 *(continued)*

Production area	Specific area	Number of identified VOS	Total content of VOS (mg/m^3)
Vulcanization	Shaper-vulcanizer	55	21,7
Finished product storehouse	Working zone	55	31,1
	Ventilation	24	7,8

The problems on toxic chemical release and carcinogen exposure during the manufacture of tyres are also considered and discussed in this reference. Particular attention is given to the qualities and types of polyaromatic hydrocarbons (PAHs) present in different types of carbon blacks and aromatic process oils. The quantity of one of the principal PAH compounds, benz(a)pyrene, was determined in the working environment in four areas of a factory, the carbon black storehouse, the mixing department, the mixing area and during transportation and mixing. The concentrations found varied between 0 mg/m^3 and 0,45 mg/m^3, with the highest levels detected in the carbon black storehouse.

The levels of N-nitrosamines formed by accelerators such as MBS, OTTBS and TMTD were determined in vulcanization fumes and remaining in the vulcanizate after curing, with the levels shown to vary between 0,1 µg/m^3 to 9,1 µg/m^3 in fumes and 10 µg/kg to 482 µg/kg in the vulcanizates. The total levels of N-nitrosamines present in the working atmosphere of different areas within the factory were also established. Levels between 2,1 µg/m^3 (buffing area), 11,65 µg/m^3 (vulcanization area) and 94,27 µg/m^3 (finished product storehouse) were found.

With respect to rubber dust, the exposures in the mixing and milling areas of tyre works in Russia were compared with those found in the United Kingdom. The values reported for the UK were shown to be lower in both cases. These workers concluded that the main causes of ambient air pollution at tyre plants were volatile organic substances, PAHs, N-nitrosamines and dust. With respect to the contribution of VOS, the composition of this component depends upon the formulation of the rubber compound, and the thermal and thermomechanical conditions of a particular process. This paper was originally published in Russian in the journal Kauchuk i Rezina[18] and this version is an English translation.

A group of industry specialists, on behalf of the EU-EXASRUB consortium, have used the rubber dust and rubber fumes data present on the European Union Concerted Action to establish exposure trends in the EU rubber industry between the 1970s and 2003.[19] The fumes and dust data present in this database has originated mainly from compliance testing, but also due to events such as the evaluation of emission controls and a part of research projects. This paper describes the detailed and comprehensive statistical modelling and analysis that was carried out and the results that were obtained. One of the overall conclusions was that the average level of exposure to rubber dust and its cyclohexane soluble fraction (i.e. rubber fumes) have declined, on average, by 4,3 % and 3,3 % (respectively) per year from the mid-1970s to 2003. This study also indicated that differences in sampling methodology, for example, the use of either glass fibre or polytetrafluoroethylene (PTFE) filters, can influence the results obtained.

Another publication related to the EU EXASRUB project has been published in the Annals of Occupational Hygiene,[20] which covers the creation of a database management system for information on occupational hygiene measurements that could be used to develop exposure models in the European rubber manufacturing industry. In a 6-month period, 59 609 measurements from 523 surveys in 333 factories from 1956 to 2003 were recorded. The database consisted primarily of measurements of N-nitrosamines, rubber dust, solvents and rubber fumes. The coding of epidemiologically relevant information was done consistently with inter-centre kappa statistics between 0,86 and 1,00. For occupational hygiene information, values of kappa statistics were estimated to be between 0,67 and 1,00. Analyses showed that coding of epidemiologically relevant information in such a multicentre, multi-country study was consistent. However, larger errors occurred in the coding of occupational hygiene information, and this was primarily caused by lack of information in the primary records of the measurements.

Vlasov, et al. of Amtel-Chernozeme published an article[21] where mathematical models were described to provide a basis for the development of an engineering procedure in the design of industrial equipment for the collection of gas emissions produced during the vulcanization processes in the tyre industry, particularly during the opening of compression moulds at the end of the vulcanization period.

Mathematical models were constructed for processes which resulted in a small amount of emissions, and for those that produced large quantities of emissions. To check the accuracy of the models, experimental data was obtained on tyre vulcanization fumes, with the levels of aldehydes, sulfur-containing compounds and aromatic compounds being monitored. One of the reasons for the need for a mathematical modelling approach is the complexity and variability of rubber fumes, with the authors estimating that the fumes from the vulcanization of tyres can contain up to 400 different components, including 12 different N-nitrosamines.

Nudel'man[22] of NIIEMI Open Joint Stock considered both the risks associated with the emissions generated during rubber manufacture and the risks that can be associated with the disposal of rubbers by methods such as incineration, e.g. the potential for the generation of dioxins from chlorinated rubbers. The situation is complicated by the large variety of vapours and gases which are emitted by the rubber, and also by the presence of aerosols which are stable, and which may condense on adjacent metal structures, so providing an ongoing source of pollution.

Nudel'man also reported on both the aerosol and gaseous components of the rubber fumes generated by some rubber compounds, including those based on NBR and a NBR/polychloroprene blends.[23] He pointed out that aerosols were formed at two stages of production, mixing (due to large mechanical stresses and local overheating) and vulcanization (due the condensation of vapours of high boiling point substances). In both cases, the aerosol particles contain numerous substances captured by the drops of oil-like material forming the aerosol. Nudel'man listed the following components that have been trapped and identified in an aerosol formed during the vulcanization of nitrile rubber (see Table 8).

Table 8 — Composition of the aerosol fraction of nitrile rubber fumes

Component	Content (%)
Dibutyl phthalate	90,0
Cyanocyclohexene	4,0
Benzothiazole	2,0
Abietic acid	2,0
p-Aminodiphenyl amine	1,0
Cyclohexanone	0,3
Carbon disulfide	0,3
p-Oxyneozone	0,2
Unidentified substances	0,2

With respect to gaseous emissions, although some are present in mixing fumes and in the stores where finished goods are kept, the greatest concentration of these is present in the atmosphere during vulcanization operations. The complexity of the composition of the gaseous fraction of rubber fumes is illustrated by an example where the vulcanization fumes generated by a NBR/polychloroprene blend was trapped and analysed and over 30 different chemical species were identified. The complexity of the chemical processes that take place during the vulcanization of rubber was illustrated by Nudel'man during a study undertaken on the volatile species produced during the peroxide vulcanization and extended post curing of a silicone rubber using the peroxide 2,4-dichlorobenzoyl peroxide. In addition to substances that were derived from the silicone polymer, such as oligomeric cyclosiloxane oligomers, and formaldehyde (an oxidation of the methyl groups), five different chlorinated aromatic compounds were detected.

An in-depth study to assess the current patterns and levels of exposure to rubber fumes and rubber process dust in the British rubber industry, and compare and contrast the data obtained from the general rubber goods, retread tyre and new tyre sectors was undertaken and results reported at the International Rubber Exhibition and Conference in 1999.[24] During the course of this work, a total of 179 companies manufacturing rubber products were visited, including 117 general rubber goods (GRG), 53 retread tyre (RT) and nine new tyre (NT) manufacturers. The survey was conducted using a questionnaire and included a walk-through inspection of the workplace to assess the extent of use of control measures and the nature of work practices being employed. In addition, the most recent exposure monitoring data for rubber fumes and rubber process dust was obtained from the companies themselves. No additional rubber dust and fumes sampling was conducted by the survey team. A comparison of the median exposures for the different manufacturing processes showed that the order of exposure to rubber fumes was as follows:

— for GRG: Moulding > Extrusion > Milling;

— for RT: Press > Extrusion > Autoclave;

— for NT: Press = All other processes.

Taking the press curing operations for the three sectors, the trend was: $P_{GRG} > P_{RT} > P_{NT}$.

The results of the study were broadly in line with those reported by other workers such as Kromhout, et al. This study by Kromhout, et al.[25] assessed the exposure to chemical substances in ten rubber manufacturing plants in the Netherlands. These plants manufactured a wide range of products (e.g. tyres. belting, hoses, extrusion products, and a range of moulded articles, including rubber to metal bonded items). The numbers of personnel in the factories ranged from 30 to 370. Personal monitoring was carried out to determine exposures to airborne particulates, rubber fumes, solvents, and degree of dermal contamination. In the case of exposure to rubber fumes, a total of 163 personal samples were taken. This compared with 666 samples for rubber dust, 137 for solvent vapours, and 669 for dermal exposure. In order to identify factors affecting the degree of exposure, the personal exposure levels and information on tasks performed, ventilation characteristics and production variables were used in multiple linear regression models. Overall, the levels of exposure over the 10 sites were found to be very variable. The level of rubber fumes exposure was found to be influenced by various factors, including curing temperature, curing pressure, and degree of local exhaust ventilation. The effect of curing different types of elastomers was not found to be statistically significant.

Donskaya, et al.,[26] in a paper looking at the ecological and health problems caused by raw ingredients used in the rubber industry, listed some of the volatile compounds that were present in the gas phase of rubber fumes where synthetic rubbers were in rubber formulation. For example,

— SBR rubbers	styrene, butadiene, ethyl benzene,
— Butadiene rubbers	butadiene, 4-vinylcyclohexene, cyclododecatriene, and
— NBR rubber	butadiene, acrylonitrile, butadiene trimers, 4-cyclohexenitrile.

The authors also referred to the generation of N-nitrosamines from the nitrosation of secondary amines formed as a result of the action of certain rubber accelerators (e.g. TMTD) and how this can be avoided. Carbon black and aromatic process oils, as sources of PAHs in rubber fumes, were also mentioned. The authors said that 14 different PAH compounds have been found in the air in Russian tyre works,[27] and that these have the potential to react with nitrogen in the air to form nitro derivatives[28] which are carcinogens and mutants.

Locati, et al. at Pirelli SpA[29] carried out a number of investigations to determine the types of PAH compounds present in compounding ingredients used in tyre manufacture, such as aromatic process oils, in extracts of compounded tyre rubbers, and in different activity areas (e.g. mixing, extrusion, calendaring, curing, etc.) tyre factories. The analysis of the process oils for 30 different PAH compounds revealed average total values for PAHs of 400 ppm (range 20 ppm to 1 534 ppm). Extraction tests on tyre rubbers that had been compounded using these oils did not detect any PAHs in the synthetic sweat media used for the extractions, i.e. there was no release of PAHs. Over 200 samples were taken in the tyre factory and the results obtained did detect the presence of PAH compounds in the cyclohexane soluble fraction of the MDHS 47 method for rubber dust and fumes (range 0,47 $\mu g/m^3$ for calendaring to 3,6 $\mu g/m^3$ for curing), but the values were well below the threshold limit values that existed at the time of this study (1993) and so the carcinogenic risk from them during tyre manufacturing was regarded as negligible. The rubber dust and fumes measurements were also below the permitted occupational hygiene limits.

Blanden and Isherwood[30] published data on rubber fumes collected at five sites in the UK that were engaged in different rubber manufacturing operations. These data are shown in Table 9.

Table 9 — Activities of the sites where monitoring took place and the rubber types being used on the sites

Vulcanization process	Rubber type
Car tyre curing	Styrene-butadiene rubber
Tyre tube curing	Butyl rubber
Injection moulding	EPDM rubber
Injection moulding	SBR/NR blend
Compression moulding	Nitrile rubber

Particulate samples were collected on glass fibre filters and an electrostatic precipitator. Tenax absorption tubes fitted with glass fibre prefilters were used to collect compounds of medium volatility. No attempt was made to collect gases or highly volatile compounds. Compounds collected on the filters were removed by extracting with methanol; and those adsorbed onto Tenax removed by extracting with diethyl ether. To simplify the interpretation of the data, prior to any analysis being carried out, each extract was separated into five fractions: basic, acidic, polar neutral, aromatic and aliphatic. In order to identify the substances present in these fractions, they were analysed by GC-MS; no quantifications were performed. The chemical analysis results showed that in all cases the fumes samples were complex mixtures of chemical substances. The most commonly occurring compound classes in each fraction of the fumes extracts are shown in Table 10.

Table 10 — Different classes of compound detected in rubber fumes

Fraction type	Main compound classes
Aliphatic	Alkanes, phenols, acid esters, phthalates
Aromatic	Aliphatic alcohols, phthalates, benzothiazoles, phenols, acid esters, phenanthrenes, and/or anthracenes, fluorenes, alkanes, sulfonic acid esters, pyrenes, chrysenes, fluoranthenes
Polar neutral	Phenols, amides, carbazoles, benzothiazoles, sulfonamides, sulfonic acid esters, phthalates, alkanes, oximes, glycols, alcohols
Acidic	Acids, alcohols, benzothiazolone, phthalates, acid esters, phenols, alkanes
Basic	Aniline, amines, imides, amides, morpholines, nicotine, phthalates, diamines, chloroalkanes

Table 10 summarizes the types of compounds that were found in the five fractions for each rubber type, but the type of rubber and the compounding ingredients present were found, as would be expected, to vary the specific chemical compounds present within each class.

These are presented in Table 11, where a selection of the extensive list of compounds that were identified for the "Basic fraction" (i.e. alkaline fraction) within the fumes collected for each of the five rubber types is given.

Table 11 — Chemical compounds detected in the "basic fraction" of rubber fumes

Rubber type	Fraction of fumes	Compounds identified
SBR	Basic	Aniline, acridine or benzoquinoline, phthalimide, dicyclohexylamine, 2-(4-morpholinyl)benzothiazole, 6PPD
EPDM	Basic	Morpholine, N-cyclohexyl formamide, cyclohexylamine, N-butyl 1-butanamide, di-isobutyl phthalate, 2-cyclohexyl benzothiazole
NBR	Basic	Dimethyl-2-butanamine, 3-(diethylamino) propane nitrile, nicotine, tetrabutyl urea, phthalates, aniline,
Butyl	Basic	Benzidine, N-(2,2-dimethylpropyl)-N-methyl benzenamine, N-ethyl-2-benzothiazolamine, benzothiazole, phenyl benzimidazole
SBR/NR	Basic	N-cyclohexylmethanamide, cyclohexyl isothiocyanate, chloroalkanes, phthalates, aniline, nicotine

The paper presented by Berg[31] at the SRC 83 Conference described the work that had been carried out using six sulfur-cured rubber/process combinations:

a) press curing of SBR;

b) press curing of chloroprene rubber;

c) press curing of nitrile rubber;

d) press curing of EPDM rubber;

e) autoclave curing of chloroprene rubber;

f) autoclave curing of nitrile rubber.

The work was carried out in two main phases. Initially, curing volatiles from the rubber formulations were investigated by Rapra using their GTM/GC-MS combination. A total of 104 different chemical species were detected in the fumes generated by the six rubber compounds, some of which were common to more than one compound, with several others that could not be identified from their mass spectra. Once the results of this phase of the work were available, personal monitoring was carried out in the workplace at the presses and autoclaves where the compounds were being cured. A range of sampling/analysis techniques had to be employed because of the large range of compounds that had been identified by the GTM/GC-MS work. In order to rationalize the work, only species that met the following criteria were targeted:

— a validated analytical method already existed;

— emitted in the highest concentrations according to the GTM/GC-MS work;

— regarded as having the biggest toxicological impact within working environments.

One of the main conclusions from the personal exposure results obtained was that in the majority of cases the individual species were below any threshold limit values (TLVs), “but because of the lack of toxicological data, it is not possible to give an exact evaluation of the impact on the working environment of this very complex mixture of compounds”.

Worwood[32] considered the origins, behaviour and subsequent interaction of airborne contamination in the rubber industry with machinery and human activity. He divided the nature of the contamination into three categories: dust, vapours, and rubber processing fumes. In latter parts of his report, Worwood cited the work by Ashworth, et al. [Report of Environmental Working Group (Dust and Fumes Control), Fort Dunlop, June 1979], which empirically identified the most important factors governing fumes evolution from rubber compounds as being

— compounding ingredients,

— processing temperature, and

— rate of exposure of fresh surface.

The work by Lawson and Newell is also cited, in which a simplified method of describing the complex mixture of materials present in rubber processing fumes are presented by classing the materials by mass or size into

— molecular hazards (0,1 nm to 6 nm), e.g. organic vapours,

— particulate hazards (0,5 µm to 8 µm), i.e. respirable particles, and

— nuisance particles (8 µm upwards).

Some of the second-category particulate hazards will be in the form of liquid particle aerosols which will condense on available surfaces.

The article goes on to consider aspects of the design of airborne contamination control systems taking into account the origin, nature and interactions.

Cocheo, et al.[33] reported the results of an industry study that involved the collection of samples in the vulcanization areas of a shoe sole factory and a tyre retreading operation. Samples were also taken in the extrusion areas of the retreading company and an insulated cable manufacturer. In all cases, the fume samples were trapped on activated charcoal, desorbed in the laboratory with trichlorofluoromethane and analysed by GC-MS. A very large number of species were identified in the four areas, with some overlapping in the chromatograms resulting in several "unidentified" peaks. An extensive table of assignments is provided for all of the individual compounds found in the four areas, together with an indication of their probable source, i.e. the rubber compound ingredient(s). The total number of compounds of each type that were identified, and quantified, in the study is shown below.

- Alkanes (16)
- Cycloalkanes (11)
- Cycloalkenes (10)
- Aromatic hydrocarbons (32)
- Chlorinated compounds (4)
- Phenols (6)
- Esters (6)
- Miscellaneous compounds (14)

  NOTE Includes ethers, sulfur and nitrogen compounds, aldehydes, alcohols, ketones, peroxides and quinones.

- Total (number of compounds = 99)

The authors concluded that charcoal is not a universal adsorbent and some compounds would not have been trapped in detectable quantities, particularly given the complex nature of the mixture which could have led to more strongly adsorbing species (e.g. hydrocarbons) displacing less strongly adsorbers. However, the study did produce results in agreement with the other studies reviewed here, in that rubber fumes are an extremely complex mix of chemicals, the composition and level of which varies according to variables such as compound formulation, process temperature, process type, and output rate.

As part of a joint occupational health program undertaken between the United Rubber Workers and major rubber products manufacturing companies in the US, the University of North Carolina undertook a study of the health hazards within four rubber tyre and tube sector companies (Goodyear, Uniroyal, Firestone and General) in a total of 50 manufacturing plants.[34] Particulate air samples were taken to assess exposure to total and respirable dust in various working areas. These samples were also analysed to determine the amount of benzo(a)pyrene present. The results obtained were found to vary from plant to plant and from different working areas within a particular plant. This study predates the establishment of a method for the determination of the rubber fumes fraction within particulate air samples and so no measurements of rubber fumes were obtained. Several samples were also taken to assess the exposure to different solvents species within the plants and an examination is made of the effects of ventilation and work practices on worker exposure to chemical agents.

The results of another study which was part of the joint occupational health program undertaken between the United Rubber Workers and major rubber products manufacturing companies in the US, was reported by workers at the Harvard School of Public Health.[35] Air sampling for total and respirable dust was undertaken in the processing, curing and tyre building areas of five tyre plants owned by two companies. These workers acknowledged that air contaminants in curing rooms included gases and vapours as well as particulates, but decided to use respirable samples as an indication of exposure to curing fumes. The exposure of a particular group of workers was found to depend upon factors such as the degree of manual handling of freshly cured tyres, and the length of cure (i.e. frequency of loading and unloading the moulds).

In a Russian study,[36] results of the determination of the composition of gaseous waste products formed in tyre production during the stage of preparation of the rubber mixes were given. The products determined include oxygen-containing and aromatic compounds, unidentified components, alkanes, resinous substances and dust.

In another Russian study,[37] gases produced during the manufacture of silicone rubber tubes for medical applications, include diethyl siloxane, hexamethyldisiloxane, hexamethylcyclotrisiloxane, octamethylcyclotetrasiloxane, the starting silicone nd-8, and also ethyl formate, methanol, ethylene and o-dichlorobenzene but in concentrations below the maximum permitted in the factory. Ventilating discharges contain principally formaldehyde and its polymers also are deposited in the ventilation apparatus. Analysis is therefore needed to monitor formaldehyde concentration only.

In 2013, ISO published a new document for the trapping and identification of volatile compounds in rubber fumes. ISO/TS 17796 describes a method for trapping and identification of volatile components of rubber fumes using active sampling on a poly(2,6-diphenylphenylene oxide) type sorbent and analysis by thermodesorption GC-MS (TD-GC-MS). The method is qualitative and identifies substances in rubber fumes; whereas, MDHS 47/2[73] provides a quantitative measure of the amount of rubber fumes in an atmosphere. To a certain extent the two methods can therefore be regarded as being complementary. In a paper presented at the International Rubber Conference in 2013, Khalfoune[74] of the LRCCP rubber and plastics research and testing laboratory described how this ISO standard had been used to determine the substances that were present in the fumes generated by some rubber compounds of known composition. This organization has also carried out laboratory studies on standard compounds of known composition and this work has provided them with the experience required to link volatile species in rubber fumes to specific compounding ingredients[75] (see 8.1.3). By making use if this experience, it was also possible for Khalfoune to link the compounds present in the fumes to the ingredient in the compound. The results that were presented by Khalfoune are summarized in Tables 12 to 15. The compound formulations are listed under each of the tables.

Table 12 — Substances identified in fumes produced by a peroxide-cured EPDM compound vulcanized at 170 °C

Substance detected in fumes	Origin in the EPDM compound
Ethylene norbornene	EPDM Vistalon 2504
Ethanol	Silane ST69
Hydrocarbon substances	Flexon 845
Ethyl palmitate	Stearic acid
Acetone	Peroximon F40
Benzenemethanol, alpha, alpha-dimethyl-	
1-[4-(1,1-dimethylethyl)phenyl]-ethanone	
1,1’(1,4-phenylene)bis-ethanone	
1[4-(1-hydroxy-1-methylethyl)phenyl]-ethanone	
Alpha, alpha’-Dihydroxy-m-diisopropylbenzene	
Triallyl isocyanate	Dial No. 7

Formulation of EPDM compound1)

EPDM Vistalon 2504	100	PEG	1,5
Carbon black N550	30	Silica VN3	20
Calcined kaolin	20	Silane ST69	0,5
Flexon 845	30	Permanax TQ	2
Zinc oxide	3	Peroximon F40	8
Stearic acid	1,5	Dial No. 7	1,5

Table 13 — Substances identified in fumes produced by a sulfur-cured EPDM compound vulcanized at 170 °C

Substance detected in fumes	Origin in the EPDM compound
Ethylene norbornene	EPDM Vistalon 2504
Ethanol	Silane ST69
Hydrocarbon substances	Flexon 845
Carbon disulfide	ZDBC
N-butyl-1-butanamine	
Benzothiazole	MBT/MBTS

Formulation of the EPDM compound2)

EPDM Vistalon 2504	100	Silane ST69	0,5
Carbon black N550	30	ZMTI	1,0
Calcined kaolin	20	Naugard 445	1,5
Flexon 845	30	Sulfur	1
Zinc oxide	3	MBT	2
Stearic acid	1,5	ZDBC	1,5
PEG	1,5	MBTS	1
Silica VN3	20		

Table 14 — Substances identified in fumes produced by an NR rubber compound at 150 °C

Substance detected in fumes	Origin in the NR compound
Alkanes	Antilux 500
Naphthalene	Carbon black
Aniline	6PPD
Methyl isobutyl ketone	

---

1) Examples of products available commercially. This information is given for the convenience of users of this document and does not constitute an endorsement by ISO of these products.

2) Examples of products available commercially. This information is given for the convenience of users of this document and does not constitute an endorsement by ISO of these products.

Table 14 *(continued)*

Benzothiazole	TBBS
Tertiary butyl amine	
Isocyanato methyl propane	
Dimethyl ethyl formamide	

Formulation of the NR compound[3)]

SMR 10CV60	100	6PPD	2
Carbon black	30	Antilux 500	1
Zinc oxide	3	Sulfur	1
Stearic acid	2	TBBS	4

Table 15 — Substances identified in fumes produced by a nitrile rubber compound vulcanized at 160 °C

Substance detected in fumes	Origin in the nitrile compound
Cyanocyclohexane	Krynac 44/50
DOS	DOS
1-Hexanol, 2-ethyl-	
Dihydrotrimethylquinoline	TMQ
Dimethylquinoline	
Aniline	6PPD
Methyl isobutyl ketone	
Diethyl amine	TETD
Diethyl formamide	
Carbon disulfide	MBTS
Benzothiazole	
Phenylmethylbenzenemethanamine	TBzTD

Formulation of the nitrile compound[4)]

Krynac 44/50	100	6PPD	2
Carbon black	95	Sulfur	0,5
Zinc oxide	3	TETD	2
Stearic acid	1	MBTS	2
DOS	25	TBzTD	3
TMQ	1		

The information presented in Tables 12 to 15 is consistent with the work that has been carried out by other workers such as Willoughby;[7][69] see 8.1.6.

[3)] Examples of products available commercially. This information is given for the convenience of users of this document and does not constitute an endorsement by ISO of these products.

[4)] Examples of products available commercially. This information is given for the convenience of users of this document and does not constitute an endorsement by ISO of these products.

8.1.3 Rubber fumes data obtained by laboratory studies

The composition of fumes that has evolved from rubber compounds when they are heated to processing temperatures using laboratory-based systems has been investigated by several workers. Majority of these studies used representative rubber compounds, with the fumes being either generated using equipment that closely resembles that used in manufacturing, or analytical equipment such as high temperature headspace generating equipment. The fumes generated by these devices is then trapped within an intermediate trapping device or transported directly into the analytical equipment. The analysis of the fumes is usually performed by a gas chromatography-mass spectrometer (GC-MS) as these devices have the dual capability of being able to separate complex mixtures of relatively low molecular weight compounds and identify them via their mass spectra. Sometimes these laboratory studies are carried out as a prelude to the trapping and analysis of fumes generated within a factory environment, as they enable a profile to be performed of the types of species that should be present within the fumes in the factory environment and so enable an effective and comprehensive sampling strategy to be devised.

Fumes produced from a wide range of rubbers were studied using these types of systems. Lucas, et al.[38] carried out laboratory investigations into the crosslinking efficiency and emissions behaviour of a number of peroxides used in EPDM-based compounds and compared the results obtained to those achieved with a TBBS-/TBzTD-accelerated sulfur-cured EPDM. The choice of peroxide was shown to be important, because using one with a high crosslinking efficiency meant that less had to be employed to achieve a successful cure with a rubber compound and so the total level of emissions, and hence moulding fumes, was lower. In addition to fogging tests to DIN 75201, the authors used thermodesorption GC-MS, as specified by the VDA 278 method, to identify the emissions that were produced by the rubber compounds, particularly the breakdown and reaction products of the peroxides. A number of principal cleavage products for five different commercial peroxides were identified and their share of the total emissions estimated. The number of compounds and their respective levels in the emissions, along with their chemical nature and molecular weight varied considerably according to the type of peroxide that was used. However, the results obtained showed fumes that it is possible to predict the range of breakdown products that will be produced by a peroxide of a known chemical structure.

Although not concerned with the direct analysis of fumes generated by peroxide cured rubbers, Nudel’man, in conjunction with Antonovski,[39] also looked into the volatile decomposition products of three commercially available peroxides used to vulcanize rubber compounds. The investigation was performed by compounding the peroxides into a common EPDM-based rubber formulation and then curing sheets of rubber at a typical moulding temperature (150 °C). This moulding process was carried out between aluminium sheets which trapped all of the volatile compounds that were formed during the vulcanization process within the rubber. Once the rubber sheets had cooled, samples were removed and placed into a thermal desorption unit that was connected to a GC-MS. The volatiles were then desorbed from the rubber by heating and identified by the GC-MS. In addition to low molecular weight substances that were unrelated to the peroxide (e.g. oligomers from the rubber, antioxidants, etc.), around ten or more different compounds were formed from each of the peroxides that were investigated in this way. The formation of cyclic compounds, such as tetrahydrofuran compounds, was thought to be due to the cyclization of intermediate breakdown products. This paper was a translation of an original published in Kauch.i. Rezina.[40]

Rozynov, et al.[41] used a mini-curing system/GC-MS combination for characterizing rubber vulcanization fumes. The system enabled the rapid screening of various rubber formulations to identify and quantify the organic compounds present in their vulcanization fumes. Some of the compounds that were detected in rubber fumes using this system were bis(2-ethylhexyl)phthalate, dimethyl formamide, carbon disulfide, acetophenone and isopropylbenzene.

A couple of studies have looked into the presence of specific species in rubber fumes. Chikishev, et al. reported the results of a Russian study[42] that described the results of experiments aimed at using mass spectrometry to determine qualitatively the accelerator and antioxidant content of gases evolved from rubber compounds heated at 75 °C. Four compounds based on SKN-26 nitrile rubber with three different types of crosslinking accelerator and two different antioxidants were used as models. Over 15 different types of compound were detected by their mass spectra and assigned, where possible, to the various antioxidants and accelerators used in the compounds.

In a German paper by Wommelsdorff, et al.,[43] trace amounts of carcinogenic PAH were found to occur in the fumes resulting from vulcanization of rubber products. Results of laboratory-based curing studies on 17 different rubber compounds based on two rubber types (EPDM and SBR) and containing different filler and oil additives which show that a reduction of the PAH content of vulcanization fumes is achievable through the use of mineral oil with low PAH levels were presented. The compounding ingredients (e.g. use of silica as opposed to carbon black) also influenced PAH emissions. Both filler and the polymer matrix, depending on their aromaticity, can reduce PAH emissions.

One of the contributing factors to rubber fumes is the low molecular weight compounds released from the base rubber at elevated temperature. Two studies, Sakdapipanich, et al.[44] and Hoven, et al.[45], looked into the volatile components released from natural rubber. These workers from Mahidol University and Chulalongkorn University used headspace GC-MS to identify the volatile compounds emitted by seven grades of raw natural rubber when heated at 60 °C for 2 h. A large range of chemical compounds were detected, and these were generated by a number of reactions as shown in Table 16.

Table 16 — Volatile chemical compounds detected in grades of natural rubber

Volatile component	Reaction mechanism
Alcohols, aldehydes, hydrocarbons, carboxylic acids	Lipid oxidation
Volatile fatty acids	Carbohydrate fermentation
Esters	Microbial esterification
Sulfur containing compounds	Amino acid degradation

The types of volatile compounds detected were found to vary according to the type of natural rubber. For example, the sulfur containing compounds found in the skim crumb rubber, which are thought to be formed due to amino acid degradation, were not found in the other six types of natural rubber. These results indicate that a wide range of compounds are present in any emissions produced when natural rubber is heated and that the types and levels present will be dependent upon the grade of natural rubber that us used in the rubber formulation.

Becklin, et al.[46][47] described how vulcanization fumes from some rubber compounds were collected directly from a laboratory scale moulding press and introduced into a gas chromatograph/mass spectrometer system for identification and quantification of the organic compounds present. Details are given of compounds detected in vulcanization fumes from NR, EPDM, SBR, polychloroprene and nitrile rubber. The introduction of the Clean Air Act in the US in 1990, focused attention on the fumes produced during rubber vulcanization as, in the absence of abatement systems, this will be released into the environment. An appreciation of the complexity of the chemical composition of rubber process fumes, and the need for companies to understand the types and levels of their emissions and what process parameters influences them, prompted this laboratory investigation by workers at the Aspen research Corporation. A laboratory-based system for studying the composition of rubber fumes, similar to the one set up by Rapra Technology, was set up. This consisted of a moulding press that was coupled to a GC-MS, and enabled a rapid screening of various rubber formulations for the identification and quantification of organic compounds present in their vulcanization fumes. The results reported in this paper were from nine different vulcanizates typically used in the industry (SBR-, NR-, NBR-, CR- and EPDM-based compounds). The effect of curing time and pressure were also investigated, as well as recipe changes within a given compound series. The analytical results on over 35 different organic compounds are presented, and the pathways for the generation of some of these chemicals are described. Three of the compounds detected (carbon disulfide, acetophenone and isopropyl benzene) are part of the list of 189 compounds that comprises the hazardous air pollutants list.

Zietlow and Schuster[48] applied analytical methods based on dynamic headspace sampling in combination with gas chromatography/mass spectrometry to the analysis of the components present in fumes generated during laboratory scale vulcanization experiments using a “heatable reactor cell” and a compression mould that simulated real workplace conditions. The results obtained from a small number of rubber compounds made it possible to identify or classify around 300 individual compounds and, in common with other studies of this type, ingredient/emission relationships were apparent, enabling the assignment of a given compound to a specific raw material. These workers found it convenient to divide the volatile compounds in the rubber fumes into two groups:

a) volatile components released from the rubber by simple vaporization, e.g. impurities in the rubber such as monomers and additives such as mineral oil and antioxidants;

b) a more "active" group of components which are primary and secondary reaction products of the crosslinking system.

Levin[49] and Asplund[50] reported on a study carried out by Trelleborg Industri AB on the composition of curing fumes released from a range of rubber compounds (four diene rubber formulations and two EPDMs) under both industrial and laboratory conditions. All five compounds were carbon black-filled with four containing typical sulfur-curing systems and one compound with a peroxide-curing system. The laboratory-based phase of the work was carried out at Rapra Technology (see 8.1.6) using their gas transfer mould/GC-MS combination. A combination of sampling media had to be used to capture fumes samples in the factory environment due to the multi-component, complex nature of rubber fumes. The following "sampling train" was used:

- adsorbent tubes for sulfur compounds;
- Tenax tubes for organic compounds;
- charcoal tubes for less volatile organic compounds;
- quartz wool filters for aerosols and particulates;
- impinger flash for amines;
- continuous registering instrument for THC.

The analysis of the fumes from the compounds resulted in the identification of 221 substances which could be divided into a number of chemical groups, including:

- aliphatic hydrocarbons;
- aromatic hydrocarbons;
- isothiocyanates;
- ketones;
- nitrosamines;
- thiazoles;
- aldehydes;
- amines;
- sulfur compounds.

This reference mentions the "Nordic Curing Fumes Project",[51] the objective of which was to investigate the effect that curing fumes have on the environment. This project was set up by the Swedish Board for Environmental Protection, supported by Norsam (the trade association of the Nordic rubber industries) and looked into the following:

- composition of curing fumes;
- environmental consequences of curing fumes;
- possibilities to control the release of curing fumes from factories.

Overall, the results showed that amines and sulfur compounds were the main compounds in the vapour phase of curing fumes from sulfur curing. Amines together with aliphatic and aromatic hydrocarbons were the main components of the vapour phase of curing fumes from peroxide curing. The emission of curing fumes contributed only slightly to the pollution in the urban environment in comparison with other sources, e.g. the traffic. Cleaning methods using oxidation (thermal and catalytic), adsorption (active carbon), absorption (scrubbing), biofiltration and condensation were studied with regard to curing fumes. The adsorption on active carbon was shown to be the most economical of the methods studied.

Aarts and Davies[52] reviewed the published information on the presence of harmful components in fumes produced during the vulcanization of rubber compounds and the conclusions reached regarding the mechanisms associated with their formation. They also reported on the results that they have produced from the analysis of fumes produced during the curing of four rubber compounds – two NR based and two oil extended SBR based – in a cure simulation apparatus that enabled continuous sampling to take place. The total amount of condensate within the system and the total volatiles produced by the four compounds were reported, with a high proportion of the condensate being due to the oil extender in the case of the SBR compounds. Major contributory components of both the condensate and the volatiles were found to be the compounding ingredient 6PPD, and the breakdown products benzothiazole and “parent” amines from the accelerators.

After reviewing various systems for analysing vulcanization fumes, Schuster, et al.[53] presented two reproducible and quantitative methods for the analysis of vulcanization fumes of rubber mixtures using laboratory curing equipment. Among the results presented the analysis results obtained on unvulcanized rubbers are presented, with over 40 different volatile compounds being detected in the vapours emitted by the NR rubber (SMR CV 50), and over 45 from the SBR rubber (Buna 1712) at 180 °C. The objective of this is to show the contribution that the base rubbers make to vulcanization fumes. The species that have been detected in the fumes of other rubbers (e.g. EPDM and CR) are also discussed. Some of the data presented has already been published by Linde in a Dissertation[54].

A collaborative paper presented by Mai (LRCC in France) and Giese (DIK in Germany)[75] at the IRC 2013 conference in Paris described the results that had been obtained by analysing rubber fumes in the laboratory using a dynamic headspace GC-MS method. To carry out the work, an EPDM compound was prepared using the formulation shown below and heated to 200°C in the thermal desorption instrument to generate fumes. The reaction products that were generated by the accelerators in the compound and detected by the GC-MS are listed in Table 17.

Table 17 — Reaction products of the accelerators detected in the fumes from the EPDM compound

Substance	Origin in the EPDM compound
Benzaldehyde	ZBEC
Benzylisothiocyanate	
N-Benzylidenebenzylamine	
Tetramethylenethiourea	TMTD
Benzthiazol	MBT
Methylthiobenthiazol	
N-Ethyl-benzthiazolamine	
Mercaptobenzothiazol	

Formulation in the EPDM Compound[5)]

EPDM – Buna AP 541	100	Zinc oxide	5
Carbon black N550	50	TMTD	1,5
Sunpar 2280	25	MBT	1,5

---

5) Examples of products available commercially. This information is given for the convenience of users of this document and does not constitute an endorsement by ISO of these products.

Mikrosol	40	ZBEC	1,5
Caloxol W3	6	Sulfur (SU 95)	1,0
Stearic acid	2		

In order to obtain a link between the substances that were detected in rubber fumes and the ingredients that were present in a compound, Mai and Giese used a methodology that involved the successive addition of ingredients to the base rubber and analysing the compounds produced using the thermal desorption GC-MS system.

This paper also included data that had been obtained on rubber fumes produced by EPDM, natural rubber and nitrile rubber compounds using ISO/TS 17796. This data is very similar to that presented by Khalfoune (also of LRCCP) at the same conference[74]; see 8.1.2 and Tables 12 to 15.

In addition, it included information on the sampling options for the collection and identification of rubber fumes in factories and the recovery rates for certain types of organic substances from different types of collection media (e.g. sorbents, filters and sampling bags). Recovery rate data are shown in 8.1.4.

8.1.4 Research on sampling and analysis techniques for rubber fumes

The complex chemical composition of rubber fumes means that ensuring that all of its components (i.e. gases, volatile compounds, aerosols, etc.) are trapped in an efficient manner to enable a full analysis to be performed is a challenging task. Accordingly, a number of workers have carried out research to obtain information on how various “sampling trains” of absorbent tubes, etc. and sampling systems can influence the data obtained. Work has also been carried out to investigate which analytical techniques and methodology offer the most effective means of identifying and quantifying the compounds present.

In two papers[55][56], Giese and co-workers at the German Institute for Rubber Technology described the development of a sampling technique, the selection and characterization of adsorbents, and the development and testing of a sampling apparatus for the sampling and analysis of vulcanization vapours and emissions. In this way, they have developed and reported on a multifaceted sampling and analysis methodology capable of collecting and then identifying and quantifying the various types of components present in rubber fumes generated in the workplace. The overall procedure has been validated for a total of approximately 50 single chemical substances. A concise summary of some of the information they provided on this multifaceted system is shown in Table 18.

Table 18 — Multifaceted sampling and analysis system for sampling rubber fumes

Substance	Collection media	Analysis Method
Highly volatile aliphatic and aromatic compounds	Activated charcoal	GC or GC-MS
Amines and amides	Silica gel	GC-NPD
Highly volatile chlorinated compounds	Activated charcoal	GC-ECD
Carbon disulfide and highly volatile sulfur compounds	Sampling bag	GC-FPD
Aldehydes and ketones	Silica gel	HPLC-UV
Low volatility compounds	XAD-2 Adsorbent	GC or GC-MS
Aerosols	Glass fibre filter	FT-IR

One of the points made is that the existence of so many different types of substances can result in one species interfering with the collection and identification/quantification of one or more of the others. In order to check on the validity and accuracy of the multifaceted system, both laboratory trials and work place monitoring at tyre and general rubber goods factories took place. A good level of reliability for the system, and accuracy of the results that were obtained using it, was demonstrated by these comparative trials. A wide diversity of single components from the following substance groups were detected in the rubber factories.

a) Highly volatile hydrocarbons

b) Amines

c) Aldehydes and ketones

d) Chlorinated hydrocarbons

e) Low volatility vapours

f) Aerosols

Several other papers have been published by the workers of the German Institute for Rubber Technology. Some of these addressed more specific components that can be found in rubber fumes. For example, a paper published in 1997[57] describes their investigations into the use of activated carbon and silica gels, surface-modified with dinitrophenyl hydrazine, were examined in terms of their suitability for sampling aldehydes and ketones in vulcanization fumes. The study demonstrates that the deriving reaction is preceded by an adsorption on the substrate material and that subsequent quantitative transformation to the hydrazone requires different reaction times depending on the reactivity of the carbonyl components.

In addition, a paper has been published which looks at the influence of plasticizer aerosols on the sampling and analysis of air pollutants in the rubber industry.[58] A sampling system for fumes and aerosols from rubber product needs to be developed with special attention to the influence of plasticizer aerosols on the sampling process itself. The efficiency of sampling with a combination of selective adsorbents in the presence of plasticizer aerosols was tested by test gas mixtures and test aerosols in tests that simulated the atmospheres that may be found in rubber factories. The analytical determination of individual substances and aerosols was carried out by gas chromatography and FTIR spectroscopy after desorption of the adsorbents with a solute. Interferences caused by plasticizer aerosols only occurred at high concentration levels.

According to a study by Cherrie, et al.,[59] another factor that needs to be taken into account when considering data obtained on rubber fumes sampled within factory environment using personal monitors, is the effect of wearing a sampling device on work practices, hence, the exposure of a worker. This carefully controlled pilot study was designed to test the hypothesis that the wearing of personal sampling pumps may affect workers' working practices and hence exposure to rubber dust and fumes and other airborne contaminants. The study made a comparison between pump samplers and the much less bulky diffusive samplers for the monitoring of exposure to organic vapours at five sites, one of them a rubber factory. The results obtained showed that at one site (a petrochemical site) the exposures were 50 % higher on the days when pump samplers were worn compared to the days when diffusive samplers were worn by the workforce. At the other sites, no differences were found and so it was concluded that the flexible nature of the work at that site, with people spending part of their day sitting down, that must play a role in the exposure that was being picked up by the pumps.

The collaborative paper presented by Mai (LRCC in France) and Giese (DIK in Germany)[75] at the IRC 2013 conference includes selective recovery rate data for a number of collection systems available for sampling rubber fumes. This information is reproduced in Table 19.

Table 19 — Recovery rates for some substances that can be present in rubber fumes

Substance/ substance group	**Collection media**	**Desorption fluid**	**Analysis method**	**Recovery** (%)
Highly volatile aliphatic and aromatic compounds	Activated charcoal	Benzyl alcohol	GC-FID (or MSD)	90,2–100
Amines and amides	Silica gel ADS	2 % KOH in methanol	GC-NPD	86,3–100
Highly volatile chlorinated compounds	Activated charcoal	Benzyl alcohol	GC-ECD	83,0–100
KOH = Potassium hydroxide				
DNPH = 2,4-Dinitrophenyl hydrazine				

Table 19 *(continued)*

Substance/ substance group	Collection media	Desorption fluid	Analysis method	Recovery (%)
Carbon disulfide, highly volatile sulfur compounds	Sampling bag	—	GC-FPD	80,0–97,5
Aldehydes and ketones	Silica gel DNPH	Acetonitrile	HPLC-UV	87,2–97,5
Low volatility compounds	XAD-2	Acetone	GC-MSD (or FID)	94,0–98,0
Aerosols	Glass fibre filter	1,1,2-tricloro-trifluoroethane	FT-IR	94,0–98,9
KOH = Potassium hydroxide DNPH = 2,4-Dinitrophenyl hydrazine				

8.1.5 Influence of rubber additives on the composition of rubber fumes

The references in the other sections illustrate how the additives in rubber compounds, along with a number of other variables, such as process type and curing temperature, can affect the composition of rubber fumes. By responding mainly to specific health and safety concerns, a number of references have highlighted how a certain class or type of ingredient can have a large contribution to the generation of specific components within the fumes, such as nitrosamines and polyaromatic hydrocarbons (PAHs). A major contributory factor to this latter category was the use of PAH-rich extender oils (i.e. the distillate aromatic (DAE) type oils) for products such as tyres. This situation has greatly altered within the last 18 months, with Directive 2005/69 coming into force on 1st January 2010 which prohibited the use of these types of additives. This development is referred to in the paragraphs relating to literature sources concerning aromatic oils and PAH compounds below.

White[60] reported that, laboratory and industrial studies of the composition of rubber fumes have shown that a proportion of the process oil within the rubber will volatilize at vulcanization temperatures and be present in the fumes. In the 1990s the highly aromatic DAE type oils were classified as “potential human carcinogens” and efforts were therefore made to develop alternatives that would create less potentially harmful process emissions. This work is now at an advanced stage and the alternatives [e.g. mild extraction solvate (MES)] are commercially available and employed in the industry.

A further two articles by White in the same volume of the European Rubber[61] also have aromatic oils as a theme. The first article by White reviews the contribution of better ingredients, working practices and fumes control equipment to ensuring that the HSE limits on rubber dust and fumes are met and that any impact on workers’ health is reduced to a minimum. In this article there is the following quote from an HSE 1993 document: “Rubber fumes are a complex and indeterminate mixture of substances”. Comments by White in the article include: Some of the chemical agents in rubber fumes are experimental or animal carcinogens, but the HSE says the complex chemistry of rubber manufacture and multiple exposures during processing make attributing a particular effect to a given exposure difficult. The COSHH approved code of practice on carcinogens applies says the HSE. Rubber fumes are absorbed by inhalation and its further metabolic fate depends on individual components. The basis for setting the HSE limit is that the critical health effect is cancer, for which a no-effect level cannot be determined.

The second article by White in this volume of the European Rubber Journal described how process oil manufacturers such as BP and Mobil were working with major rubber companies such as Avon to produce less toxic oils (e.g. containing lower amounts of PAH compounds) which would in turn reduce the toxicity of rubber fumes. Studies at the time were undergoing to determine how much the process oil in a rubber compounds contributed to the total amount of rubber fumes generated during high-temperature processes such as vulcanization.

The presence of nitrosamines in rubber fumes has generated a lot of interest for many years and Mukhutdinov and Mukhutdinov[62] reviewed the mechanistic chemistry associated with a range of phosphorus-based compounds that can be used as alternatives to traditional, potentially N-nitrosamine generating accelerators for sulfur cures and which, in some cases, can also be used to extend scorch times and improve ageing resistance. These types of additives would therefore reduce the occurrence of N-nitrosamines in vulcanization fumes and as residual species in vulcanizates.

Another approach to reducing the potential toxicity of rubber fumes from N-nitrosamines is covered by Ferradino and Zukowski of the Vanderbilt company.[63] Vanderbilt developed a thiuram and a dithiocarbamate accelerator which contain four isobutyl groups. The steric hindrance that these groups provide means that any di-iso-butylamine formed by their chemical breakdown during vulcanization is less likely to react with nitrosating agents such as NO_x to form the N-nitrosamine. Another factor that comes into play is the fact that the isobutyl groups reduce the volatility of the amine break down product (in comparison to amines formed from more common thiurams and dithiocarbamates) and make any reaction with a nitrosating agent in the process atmosphere less likely.

An early article by Davis[64] in 1988 commented on stringent new guidelines for N-nitrosamine recently introduced by the German government, includes a description of work carried out by the German occupational safety and health authorities, in which they carried out sampling work in 545 work environments during 1987 and identified seven different types of N-nitrosamines:

a) N-nitrosodimethylamine;

b) N-nitrosodiethylamine;

c) N-nitrosodibutylamine;

d) N-nitrosomorpholine;

e) N-nitrosopiperidine;

f) N-nitrosomethylphenylamine;

g) N-nitrosoethylphenylamine.

Since that date, a number of changes have occurred in rubber compounding technology, leading to the development of new accelerators that either have secondary amine breakdown products that are less likely to form nitrosamines, or will not form any nitrosatable breakdown products at all.

Other areas where the specific influence of a particular systems (i.e. cure systems) or compounds on the composition of rubber fumes has received attention, both in the area of tyre production, are the coupling agents used to improve the reaction between the silica filler and the rubber, and the use of resorcinol to coat steel cords.

The first of these, coupling agents, are one of the specific things that contributes to the overall fumes and volatiles generated during tyre manufacture. During the coupling reaction, which occurs during the mixing and compounding phase of the process volatile, low molecular weight compounds such as ethanol are evolved as by-products. To address this particular issue, manufactures such as GE Advanced Materials are developing novel low-volatile organic content silane coupling agents.[65]

Another paper which addresses this area, is the one presented by Dierkes and Noordermeer[66] at the IRC in 2005, where they described the development of a mathematical model for ethanol and its devolatilization from rubber compounds containing silica and silanes during the internal mixing stage. This devolatilization is essential if efficient coupling between the silica and the polymer is to be achieved. Mass transfer between the surface layer of the polymeric material and the vapour phase is considered to be the main contributor towards devolatilization.

In the case of resorcinol, the effect of predispersed resorcinol in the coating compound of brass-plated steel cord for radial tyres has been studied by workers at the Hualin Group[67] by comparison with the conventional resorcinol. The results showed that the predispersed resorcinol could be added in the final mixing stage because of its high dispersion in rubber compound, thus eliminating the fumes and strong odour generated by conventional resorcinol during mixing at elevated temperatures. The predispersed resorcinol had no adverse effect on the physical properties of rubber compound and good adhesion between predispersed resorcinol-containing compound and steel cord was obtained.

To address the influence of rubber chemicals in general, a project was set up by the Swedish Environmental Protection Agency in 1991,[68] the aim of which was to study the environmental impact from all rubber chemicals from the fumes generated by the rubber industry. The rubber industry contributed to this document by providing information on around 800 chemicals, and one of the conclusions was that the industry had improved the way that it was working over the years by substituting chemicals that caused concern with safer ones, or eliminating the chemicals altogether.

8.1.6 Work carried out at Rapra Technology Ltd.

A considerable amount of the fundamental scientific work that has been carried out on the nature and composition of rubber vulcanization fumes has been conducted by Rapra Technology. These studies, which began in the 1970s and carried on through into the late 1990s were led by Dr. Bryan Willoughby. The results that were obtained and the understanding of the chemical relationships that resulted enabled the composition of rubber fumes from a given rubber compound to be predicted with a high degree of accuracy. One of the principal approaches that were taken was to carry out a series of over 40 vulcanization experiments, using industrially relevant formulations, in a specially designed apparatus [the Gas Transfer Mould (GTM)] using a "pool" of 75 ingredients and studying the species that were given off in the fumes by interfacing the GTM with a GC-MS. More than 150 different chemical species were detected and these enabled ingredient/process conditions/emission relationships to be identified, for example:

- a list of all the formulations which yield a single emission and those that yield more than a certain amount of a specific emission, the common ingredients in such lists of formulations;
- a list of all the formulations which use a specific ingredient; and the common emissions from such a list of formulations;
- the overall effect of the formulation, the curing temperature and the temperature of the rubber at the time of analysis.

The complexity of industrial rubber mixes meant that the relationship between the ingredients and the emissions obtained was not necessarily simple. For example, an individual component of rubber fumes may have more than one source in a formulation. The work at Rapra did reveal certain key trends however. For example, three distinct sources of volatile emissions were recognized:

- volatile ingredients, e.g. antioxidants and plasticizers;
- volatile impurities of ingredients, e.g. residual monomers and manufacturing impurities;
- volatile by-products of chemical reactions, e.g. vulcanization and antioxidant reactions.

Among the information provided by this in-depth paper[7] are sections on the origin of specific individual compounds, such as carbon disulfide, and a table which lists the potential origins of over 40 volatiles species which can be detected in rubber fumes. The results of the Rapra Vulcanization Project, and a description of the predictive rubber fumes software that resulted from it, have also been presented in a Rapra publication.[69]

In addition to these summary publications, a large number of other papers and publications have been published by Willoughby and other workers at Rapra during the course of their work in rubber fumes. For example, in a paper entitled "Prediction of On-site Performance for Vulcanization Fumes" RWB Smith and BG Willoughby[70] described rubber fumes as being comprised of two distinct phases:

a) visible portion, composed of aerosols formed by the condensation of hot vapours, which can be trapped onto filters providing that the sampling flow rate is high enough;

b) invisible portion, composed of a complex mixture of species that remain in the gaseous phase. The wide range of species present mean that either a range of adsorbents, or a range of liquid media for trapping by absorption have to be used to ensure that the data subsequently obtained by analysis is fully representative.

The paper goes on to describe work carried out using the GTM/GC-MS configuration to predict the range of species that will be present in factory fumes as an aid to putting together trapping protocols for the gaseous species; the GC-MS analysis of fumes collected on a single adsorbent (Tenax) in a rubber factory when the same rubber compound is being vulcanized; and analysis by GC-MS of the aerosol fraction released from hot rubber after vulcanization using a laboratory sampling device. Other papers of interest include: Control at source for Vulcanization Fumes, BG Willoughby, Health and Safety in the Plastics and Rubber Industries.[71]

In an earlier review by Willoughby,[1] data obtained on the composition of rubber fumes, recorded using laboratory-based experiments with the Rapra GTM/GC-MS combination, are provided which illustrate how the processing temperature can affect the types of hydrocarbon species detectable in fumes released from rubbers containing SBR, and the relative levels of these species. These data are shown in Table 20.

Table 20 — Influence of temperature on the concentration of specific chemical compounds detected in rubber fumes

Extrusion (up to 110 °C) µg/m^3	**Hydrocarbon compound in fumes**	**Vulcanization 1 (at 145 °C to 165 °C)** µg/m^3	**Vulcanization 2 (at 180 °C to 240 °C)** µg/m^3
25–180	Benzene	10–1 200	8–15
20–160	Toluene	6–800	4–8
1–20	Styrene	2–180	90–500
1–15	Ethylbenzene	2–90	30–150
0–3	4-Vinylcyclohexene	ND	30–210
0–10	Isopropylbenzene	2–200	60–250
0–7	Di-isopropylbenzene	1–75	35–70
0–20	Dodecenes	5–180	300–7 000
1–10	Cyclododecatriene	5–400	ND
D = Detected but not quantified ND = Not detected			

In a relatively early Rapra paper,[2] Maisey described the work that had been carried on rubber fumes using the GTM/GC-MS combination and specifically reports the results that have been obtained on the effect that changing the moulding temperature has on the amount of a particular reaction product (carbon disulfide) released from a sulfur-cured EPDM rubber containing the accelerator TMTD. Results showed that increasing the temperature in steps, from 150 °C to 200 °C and finally 250 °C, increased the amount of carbon disulfide released from 1,03 m.mole to 1,91 m.mole and finally to 2,34 m.mol. This work by Rapra has also shown that by modifying the cure system, no carbon disulfide is liberated.

The effect of temperature on the amount generated of a particular compound is also commented with respect to the amount of TDI liberated from a urethane adduct curing agent for NR compounds.[3] The amount of free TDI found in the vulcanization fumes was found to reduce as the temperature was reduced from 200 °C to 153 °C. Different levels of free TDI were also found for the same compound above a mixing mill and above a moulding press, showing the effect that different processes and processing conditions can have.

Another Rapra paper[4] included a brief table showing how the total amount of rubber fumes, determined as total weight loss, varies with vulcanization temperature.

- at 160 °C, 0,18 %
- at 175 °C, 0,5 %
- at 190 °C, 0,75 %

8.2 Other sources of information

8.2.1 General

The following databases were searched.

a) **Chemical Abstracts Service (CAS)**, a division of the American Chemical Society

CAS is the most authoritative and comprehensive source for chemical information. CAS databases, including CAS REGISTRYSM, the gold standard for substance information, are curated and quality-controlled by CAS scientists. Combining these databases with advanced search and analysis technologies, CAS delivers the most complete, crosslinked, and effective digital information environment for scientific research and discovery.

The CA SEARCH®: Chemical Abstracts® database includes over 20 million citations to the worldwide literature of chemistry and its applications from 1967 forward.

b) **Pollution Abstracts (POLLUAB)**

POLLUAB is a bibliographic database from Cambridge Scientific Abstracts that contains information on air, land, marine, and freshwater pollution, their sources, and their control. Sewage and wastewater treatment are covered, as well as water management. Both scientific research and government policies on environmental information are included. POLLUAB corresponds to the printed publication Pollution Abstracts. This database contains more than 376 391 records, around 12 000 new records per year, and dates from 1970 to the present.

c) **NTIS database**

Containing over 2 million bibliographic records, the NTIS Database is the preeminent resource for accessing the latest research sponsored by the United States and select foreign governments. The database represents billions of dollars in research, which includes research reports, computer products, software, video cassettes, audio cassettes and more. The complete electronic file dates back to 1964 and most records include abstracts. On average, NTIS adds over 30 000 new records per year to the database.

d) **Other external databases**

In addition to the three external databases that were searched, other databases were considered, but not searched as they were not thought to be cost-effective ways of obtaining information that was useful to the project. These were:

- toxcentre;
- embase;
- healsafe;
- chemsafe.

8.2.2 Search strategy for external databases

To ensure that this part of the project was carried out in a cost-effective way, an interactive approach between the information scientists and the rubber consultants was taken. This enabled a targeted initial search to be undertaken, the results of which were then checked to ensure that the right type of article was being found and then the search refined and another carried out. In addition to controlling costs by ensuring that time on the database was used efficiently, titles only were obtained initially and then those that were of interest selected for the purchase of the abstracts. This procedure was carried out a number of times to ensure the best chance of finding articles of relevance.

8.2.3 Chemical abstracts results

The search strategy for this database was refined many times to optimize its effectiveness. A few hundred titles were obtained and examined, and full abstracts purchased for over 30 articles. These abstracts, which were in English, showed that around 10 of the articles were in German, Chinese, Japanese or Russian.

8.2.4 General POLLUAB and NTSI database results

a) Both of these databases were searched a number of times to refine the strategy to ensure optimum results.

b) These databases were included in the searching activities undertaken for the project as it was thought that they may contain articles that addressed the composition and nature of rubber process fumes. However, the results obtained were only indirectly relevant, with most of the focus being on emissions (e.g. VOC and dust) to atmosphere from the rubber factories and the reporting of the results of studies which addressed occupational hygiene and genotoxicity issues.

8.2.5 Search of industry-relevant publications, government publications and relevant websites

The websites of prominent government agencies were accessed and searched for relevant information.

a) UK Government Health and Safety Executive (HSE) website (www.hse.gov.uk)

The following publications were among those that were found:

A new practical guide to complying with COSHH in the rubber industry — Guidance HSE Books 1997 **ISBN 0 7176 1372 0**

Control of rubber fumes at extruders, calenders and vulcanizing operations — Guidance HSE Books 1994 **ISBN 0 7176 0783 6**

Maintenance, examination and testing of local exhaust ventilation HSG54 — (Second edition) HSE Books 1998 **ISBN 0 7176 1485 9**

An introduction to local exhaust ventilation HSG37 (Second edition) HSE — Books 1993 **ISBN 0 7176 1001 2**

The selection, use and maintenance of respiratory protective equipment: A practical guide HSG53 (Second edition) HSE Books 1998 **ISBN 0 7176 1537 5**

Safe to breathe: Dust and fumes control in the rubber industry Leaflet IACL95 — HSE Books 1995 **ISBN 0 7176 0979 0**)

Controlling airborne contaminants in the workplace Technical Guide TG7 British Occupational Hygiene Society 1987 **ISBN 0 9059 2742 7**

A small survey of exposure to rubber process dust, rubber fumes and N-nitrosamines, Research Report RR819, Prepared by the Health and Safety Laboratory for the Health and Safety Executive, 2010

b) The EU website and the Council of Europe website

Both of these websites were searched via the home page search box using appropriate keywords but no relevant documents could be found.

c) Other websites

The World Wide Science website was searched using terms such as “rubber emissions” and “rubber fumes”.

Several relevant articles were found, but these had already been detected using the various database searches. Other articles that were found included various UK government guidance documents on the control of rubber dust and rubber fumes.

d) Search of other sources (e.g. trade and research associations)

British Rubber Manufacturers Association (BRMA), later divided into the British Tyre Manufacturers Association (BTMA) and the British Rubber and Polyurethane Products Association (BRPPA).

e) Other information sources

In addition to the databases and sources described above, other sources of information have been consulted, including the following:

- Rapra Review Reports, e.g. Health and Safety in the Rubber Industry by Naesinee Chaiear;
- books, e.g. Rubber Fumes — Ingredient/Emission Relationships (by Bryan Willoughby), Nitrosamines in Rubber (by B.G. Willoughby and K.W Scott) and Air Monitoring in the Rubber and Plastics Industries (by B.G Willoughby);
- government publications, e.g. those published by the UK Health and Safety Executive;
- information obtained during the managing of research projects, e.g. Rubber Breakdown Products Project conducted for the UK Food Standard Agency from 2002 to 2005 and the Rapra Rubber Fumes Project that ran during the 1980s.

9 Summary of the finding of the literature review

This clause gives a summary of the overall findings of the literature search, with additional specific summaries of the results provided in Clauses 6 and 7.

A substantial literature search has been undertaken. This has enabled a wide range of articles and information sources to be consulted, including peer-reviewed papers in scientific journals, articles published in trade journals, books, best practice guides, research project results, and conference proceedings. These articles have shown that information has been published in a number of geographical areas, in particular the US, the Far East, Russia and the EU.

These articles have shown that rubber fumes has a very complex chemical composition, both in terms of the types of chemical compounds present (usually over 30 for a typical rubber compound) and the physical forms (e.g. gases, volatile compounds and aerosols) that these chemicals are in. They have also shown how changes in rubber technology over the past 40 years will have altered the composition of rubber fumes and will have increased the level of protection for workers in the rubber industry.

The following salient points have been obtained from the articles and papers that have been obtained and examined.

a) The specific processing conditions (e.g. the precise moulding temperature) will influence the levels and types of species present in the curing fumes of a particular rubber compound.

b) In the case of certain “high-risk” species (e.g. nitrosamines and polyaromatic hydrocarbons) it has been shown that their presence and actual levels in rubber fumes are very dependent on the starting ingredients present in the original compound.

c) Within a particular rubber factory, the types and overall levels of species in the process fumes varies according to the type of process being carried out, i.e. mixing, extruding, moulding, storage, etc. For example, in the general rubber goods sector the overall level of exposure to rubber fumes has been found to vary as shown below:

   Moulding > Extrusion > Milling

d) Rubber process fumes comprise a wide range of chemical species with respect to molecular weight and polarity. A number of studies have reported over 30 different species in the fumes from a particular rubber compound, and the extensive work carried out by Rapra Technology has shown that over 150 different chemical species could be detected in the fumes generated by the vulcanization of 40 different compounds using a “pool” of 75 compounding ingredients. The species present in rubber fumes have been shown by a number of workers to fall into one of a wide range of chemical groups:

   1) aliphatic hydrocarbons — straight chain and cyclic;

   2) aromatic hydrocarbons;

   3) halogenated compounds;
   4) isothiocyanates;
   5) ketones;
   6) nitrosamines;
   7) thiazoles;
   8) aldehydes and alcohols;
   9) esters and ethers;
   10) amines and nitosamines;
   11) sulfur compounds.

e) The work carried out by Rapra Technology has shown that there are three distinct sources of volatile emissions:
   1) volatile ingredients, e.g. antioxidants and plasticizers;
   2) volatile impurities in ingredients, e.g. residual monomers and manufacturing impurities;
   3) volatile reaction and breakdown products of chemical reactions that occur during processing, e.g. vulcanization and antioxidant activity.

   The relative contribution of these to any given sample of rubber fumes are dependent on the ingredients present in each rubber formulation contributing to the fumes present in a working atmosphere in a particular moment in time.

f) The wide range of species that can be detected in rubber process fumes (listed in point 4) i present in a number of physical forms, for example gases, vapours and aerosols. The relative levels of these different physical forms vary according to the different areas (e.g. mixing, moulding, storage, etc.) present within a rubber factory.

g) In common with all technologies, rubber technology has evolved over the years and the changes have had a direct effect on the composition of rubber fumes. One of the main drivers for this change has been health and safety legislation and this is believed to have benefitted the health of the workers in the industry by reducing their exposure to potentially hazardous substances.

10 Conclusions

The aim of this literature review was to evaluate, on a basis of sound scientific literature, whether or not it is scientifically robust to consider “rubber fumes” as a homogeneous entity from a chemical point of view, and more importantly in relation to measurement and control of occupational exposure risk for the rubber industry as a whole.

The results that have been obtained by this comprehensive study confirm that rubber fumes are a very complex mix of chemical substances which have a wide range of possible sources and origins. Authoritative examples in the literature that illustrate this situation are cited in this document, for example where monitoring of rubber fumes has taken place at sites where rubber products are manufactured,

In addition to the large range of chemical species that can be present in rubber fumes, this study has shown that the physical form (i.e. gases, vapours or aerosol) that these species exist in the factory environment can be influenced by the type of process being carried out and the process temperature.

This review confirms that the type of process (e.g. moulding, calendering, etc.) and the processing temperature can also influence the reactions that take place in a rubber compound and, hence, the types of species that can be emitted, in addition to the proportion of the rubber compound which falls within the “volatile fraction” and so has the potential to be emitted as process fumes.

The studies that have been carried out and included in this document have therefore shown that, even when the detailed composition of a rubber compound being processed is known, it is difficult to compile a predictive list of those species that are likely to be present in its process fumes. It is difficult to provide this comprehensive assessment, as there are many variables that influence the composition of rubber fumes, and that is why methods that have been developed for the measurement of rubber fumes have targeted a particular fraction of the fumes (e.g. the “visible portion” in the case of the HSE’s MDHS Method 47) for quantification and have not attempted to carry out a more detailed analysis of what that fraction is actually comprised of.

Based on the information derived from this study into rubber fumes and that of our own research into the subject, it is our considered opinion that the fumes emitted from rubber should not be considered as a single chemical entity, but as a highly complex mixture of chemical species which varies depending upon the composition of the rubber compound, the processes by which it is manufactured and the temperatures to which it is exposed during those processes.

It has been highlighted that rubber products are made from rubber formulations which can be very complex in the type, range and levels of the ingredients contained within them. As a result it is possible to produce an almost many number of rubber formulations for a given application or product, which in turn will add to the diversity of the possible volatile chemical species evolved during their manufacture.

Although the rubber industry is now over 100 years old, research and development work still continues, with objectives constantly under revision to meet current and projected needs and new legislation. Existing rubbers continue to be modified, new process methods developed, new additives adopted and novel products designed. As a result of these and changes due to legislation, such as the EU Directive 2005/69 (replacement of PAH-rich aromatic extender oils), and reduction in the use of nitrosamine forming additives over more recent years, the composition of rubber fumes has changed and is likely to continue to change as further progress is made in the rubber industry. These changes have resulted in improvements in the protection of workers in the rubber industry, as have other technological changes, such as the movement away from open mill mixing to the use of internal mixers, which has reduced their overall exposure to rubber fumes by around 4 % per annum since the 1970s.

Annex A
(informative)

Abbreviated terms

ACM	acrylic rubbers
AEM	ethylene-acrylic terpolymer
AU	polyester type polyurethane rubbers
BR	rubber based on butadiene
CIIR	chlorobutyl rubber
CM	chlorinated polyethylene
CO	epichlorohydrin homopolymer
CPE	chlorinated polyethylene
CR	chloroprene rubber
CSM	chlorosulfonated polyethylene
EACM	ethylene-acrylic terpolymer
EAM	ethylene-vinyl acetate
ECO	epichlorohydrin copolymer with ethylene oxide
EPDM	ethylene-propylene terpolymer
ETER	epichlorohydrin terpolymers
EU	polyether urethane
EVA	ethylene-vinyl acetate
FKM	fluorocarbon rubber
FPM	fluorocarbon rubber
FVMQ	fluoro vinylmethyl silicone
HNBR	hydrogenated nitrile rubber
MBT	mercaptobenzothiazole
MBTS	dibenzthiazyldisulfide
NR	natural rubber
PAH	polycyclic aromatic hydrocarbon
PVMQ	phenyl vinyl methyl silicone

SMR	Standard Malaysian Rubber
TBBS	*N*-*tert*-Butyl-2-benzothiazole sulfonamide
TETD	tetraethyl thiuram disulfide
TBZDT	tetrabenzyl thiuram disulfide
TMTD	tetramethyl thiuram disulfide
TMQ	polymeric 2,2,4-trimethyl-1,2-dihydroquinoline
VMQ	vinyl methyl silicone
ZDBC	zinc dibutyl dithiocarbamate

Bibliography

[1] Willoughby B.G. Chapter on Health and Safety. In: *Developments in Rubber Technology — 4*, (Whelan A., & Lee K.S. eds.). Elsevier Applied Science, 1987, pp. 253–306.

[2] Maisey L.J. SRC-81 Conference Proceedings, Helsinki, May 21-22, p.215-26, 1981

[3] Davey J.E., & Edwards A.D. Analyst 108, No 1284, p 407- 411, March 1983

[4] Willoughby B.G. Health and Safety in the Plastics and Rubber Industries, Conference Warwick, Sept. 19 – Oct 1, p12.1-12.9, 1980

[5] Grassie N., & Scott G. *Polymer Degradation and Stabilisation*. CUP, 1985

[6] Davies A.G. *Organic Peroxides*. Butterworths, London, 1961

[7] Willoughby B.G. Paper 7, Hazards in the Rubber Industry, Shawbury, 28-29th September 1999

[8] Coran A.Y. In: *Vulcanization, Science and Technology of Rubber.* (Eirich F.R. ed.). Academic Press, New York, 1978

[9] Shershnev V.A. *Rubber Chem. Technol.* 1982, **55** p. 537

[10] Pilati F., Masoni S., Berti C. *Polym. Commun. (Guildf.)*. 1985, **26** p. 280

[11] Pospisil J. *Aromatic Amine Antidegradants, Developments in Polymer Stabilisation — 7.* Elsevier Applied Science, London, 1984

[12] Ashness K.G., Lawson G., Wetton R.E., Willoughby B.G. *Plast.Rubb.Proc.Appl.* 1984, **4** p. 69

[13] Saunder K.J. *Organic Polymer Chemistry.* Chapman and Hall, London, 1973

[14] Crafts R.C., Davey J.E., McSweeney G.P., Stevens I.S. *J.Nat.Rubber Research*. 1990, **5** p. 275

[15] Willoughby B.G., & Scott K.W. *Rubber Chem. Technol.* 1998, **71** p. 310

[16] Willoughby B.G., & Scott K.W. *Rubber Chem. Technol.* 1998, **71** p. 310

[17] Frolikova V.O., Donskaya M.M., Yalovaya L.I., Pichugin A.M., Vishnyakov I.I. *International Polymer Science and Technology*. 2009, **36** (8) pp. 29–36

[18] Frolikova V.O., Donskaya M.M., Yalovaya L.I., Pichugin A.M., Vishnyakov I.I. *Kauchuk i Rezina*. 2008, **5** pp. 20–27

[19] De Vocht F., Vermeulen R., Burstyn I., Sobala W., Dost A., Taeger D. et al. *Occup. Environ. Med.* 2008, **65** (6) pp. 384–391

[20] De Vocht F., Straif K., Szeszenia-Dabrowska N., Hagmar L., Sorahan T., Burstyn I. et al. *Ann. Occup. Hyg.* 2005, **49** (8) pp. 691–701

[21] Vlasov G.Y., Syritsyn L.M., Chemerinskii V.B. International Polymer Science and Technology, 32, No.5, p. T/41-7, 2005 (translated from Kauchuk i Rezina, No.5, 2004, p.15-22)

[22] Nudelman Z.N. IRC 2002. Conference Proceedings, Prague, 1st-4th July 2002, Paper 90, pp.9, 2002

[23] Nudel'man Z.N. *International Polymer Science and Technology 28*, No.2, p.T/38-42, 2001

[24] Dost A.A. D. Redman D and G., International Rubber Exhibition and Conference 1999, Environment Paper 5, Manchester, 7th-10th June 1999

[25] Kromhout H., Swuste P., Boleij J.S.M. *Ann. Occup. Hyg.* 1994, **38** (1) pp. 3–22

[26] Donskaya M.M., Kavun S.M., Krokhin A.V., Frolokova V.G., Khazanova Yu.A. *International Polymer Science and Technology 21*, No.3, p.T/38-44, 1994 (Translation of Kauchuk i Rezina, No.5,1993, p.37)

[27] Rogszewska T. et al. *Pol. J. Occup. Med.* 1989, **2** (4) pp. 366–375

[28] Schuster R.H. et al. *Kautsch. Gummi Kunstst.* 1990, **43** (2) pp. 95–106

[29] Locati G., Consonni G., Fantuzzi A. IRC ‘93-144th Meeting, Fall 1993, ACS, Rubber Div., 26th-29th Oct.1993, Paper 14, p.13

[30] Blanden C.R, & Isherwood S. A. Health and Safety in the Plastics & Rubber Industries, York,15-16 Sept.1987,p.3/1-3/10

[31] Berg H. SRC 83. Technological Advances — Structural Implications; Proceedings of the 7th Scandinavian Rubber Conference Editor(s): May 19-20, 1983, p.565-82

[32] Worwood J.A. *Plastics and Rubber Processing and Applications.* 1984, **4** (4) pp. 331–336

[33] Cocheo V., Bellomo M.L., Bombi G.G. *Am. Ind. Hyg. Assoc. J.* 1983, **44** (7) pp. 521–527

[34] Harris R.L, Arp E.W., Symons M.J., Van Ert M.D., Williams T.M. ACS, Rubber Div. Fall Meeting. Cleveland, Ohio. *Paper.* 1977 Oct., **40** p. 61

[35] Burgess W.A., Di Berardinis L., Gold A., Treitman R. ACS,Rubber Div. Fall Meeting Cleveland,Ohio. *Paper.* 1977 Oct., **39** p. 10

[36] Zinchenko V.M., Koval’chuk B.V., Prigunova S.N., Rudoi Yu S. *Kauchuk i Rezina* (USSR) No.10, p.33-4, 1982

[37] Novokovskaya M.I., Saltanova V.B., Shaposhnikov Yu.K. *Kauchuk i Rezina* (USSR) No.6, p.48-9, 1976

[38] Lucas G., & Giese U. *Kautsch. Gummi Kunstst.* 2008, **61** (4) pp. 180–187

[39] Nudel’man Z.N., & Antonovskii V.L *International Polymer Science and Technology, 21*, No.1, 1994, p.T/52-4

[40] Nudel’man Z.N., & Antonovskii V.L. *Kauchuk i Rezina*, No. 6, p.14, 1993

[41] Rozynov B.V., Liukkonen R.J., Becklin D.O., Noreen A.L., Ponto S.D. Polymer Preprints. Volume 41, Number 1. Proceedings of a conference held in San Francisco, Ca., March 2000. Editor(s), ACS, Div. of Polymer Chemistry, 2000, p.692

[42] Chikishev Yu. G., Klyuev N.A., Vakhtberg G.A., Zhil’Nikov V.G. *Kauchuk I Rezina* (USSR), No.12, p.42-3, 1975

[43] Wommelsdorff R., Giese U., Thomas C., Hill A. *Kautsch. Gummi Kunstst.* 1994, **47** (8) pp. 549–555

[44] Sakdapipanich J., & Insom K. *Kautsch. Gummi Kunstst.* 2006, **59** (7-8) pp. 382–387

[45] Hoven V.P., Rattanakaran K., Tanaka Y. *Rubber Chem. Technol.* 2003 Nov.- Dec., **76** (5) pp. 1128–1144

[46] Becklin D., Herman T., Ponto S., Rozynov B. Rubber and Plastics News 25, No.2, p.15/8, 1995

[47] Becklin D., Herman T., Ponto S., Rozynov B. 147th Meeting, Spring 1995, ACS Rubber Div. Philadelphia, Pa., 2nd-5th May 1995, Paper 31, pp.14

[48] Zietlow J., & Schuster R.H. IRC ‘93-144th Meeting, Fall 1993, ACS, Rubber Div. Orlando, Fl., 26th-29th Oct. 1993, Paper 10, pp.8

[49] Levin N.M. IRC ‘93-144th Meeting, Fall 1993, ACS, Rubber Div. Orlando, Fl., 26th-29th Oct. 1993, Paper 11, p.13

[50] Asplund J. *Kautsch. Gummi Kunstst.* 1995, **48** (4) pp. 276–280

[51]. Internal Report from the Nordic Rubber Industry 1991. *Summary Kautsch, Gummi Kunstst, Vo.* 1993, **46** p. 858

[52] Aarts A. J., & Davies K.M Rubbercon 92 — A Vision for Europe, PRI Brighton,15th-19th June 1992,p.455-60

[53] Schuster R.H. H. Linde H and G. Wuensch. *Kautsch. Gummi Kunstst.* 1991 March, **44** (3) pp. 222–231

[54] Linde H. Untersuchung von bei der Vulkanisation enstehenden Gasen und Dampfen, Dissertation, Universitat Hannover (1990))

[55] Giese U. Hazards in the European Rubber Industry. Conference proceedings Manchester, 28th-29th Sept. 1999, Paper 9

[56] Giese U., Will T., Stanetzek I., Schuster R.H. *Gummi Fasern Kunstoffe.* 1997, **50** (7) pp. 567–574

[57] Kuhn-Stoffers P., Giese U., Schuster R.H., Wunsch G. *Kautsch. Gummi Kunstst.* 1997, **50** (5) pp. 380–385

[58] Will T., & Giese U. *Kautsch. Gummi Kunstst.* 1996 March, **49** (3) pp. 200–205

[59] Cherrie J.W., Lynch G., Bord B.S., Heathfield P., Cowie H., Robertson A. *Ann. Occup. Hyg.* 1994, **38** (6) pp. 827–838

[60]. *European Rubber Journal*. 1998 Sept., **180** (9) p. 39

[61] *European Rubber Journal*, 176, No.2, Feb. 1994, p.24-25 and 27-8

[62] Mukhutdinov A.A., & Mukhutdinov E.A. International Polymer Science and Technology 24, No.7, p.T/54-63, 1997

[63] Ferradino A., & Zukowski R. *Rubber and Plastics News*. 1996 Nov. 4th, **26** (7) pp. 14–16

[64] *European Rubber Journal.* 1988 Sept., **170** (8) p. 29

[65] Joshi P.G. Tire Technology International Annual Review 2005, p.126-9

[66] Dierkes W., & Noordermeer J.W.M. IRC 2005: North European International Rubber Conference held Maastricht, The Netherlands, 7th-9th June 2005, p.315-25

[67] Li B., Li H., Wang G., Gongye L. 19, No.8, p.456-8, 1999

[68] Ringstrom A Rubbercon ‘95. *Paper.* 1995 May 9th-12th, **F2** p. 10

[69] Willoughby B. Rubber Fumes: Ingredient/Emission Relationships. *Rapra Technology Ltd*. 1995, **1994** p. 105

[70] Worwood J.A. Health and Safety in the Plastics & Rubber, 3rd International Conference, 15-16 Sept. 1987,p.4/1-4/9

[71] Willoughby B. SRC 85.New Technology for Improved Design with Rubber, Copenhagen,Denmark, June 10-12, 1985,p.593-607

[72] ISO/TS 17796, *Rubber — Trapping and identification of volatile components of rubber fumes with active sampling on a poly(2,6-diphenylphenylene oxide) type sorbent, using thermodesorption and gas chromatographic method with mass spectrometric detection*

[73] Health and Safety Executive. *MDHS 47/2 (Methods for the Determination of Hazardous Substance) — Determination of rubber process dust and rubber fumes (measured as cyclohexane-soluble material) in air.* HSE, UK, 1999

[74] KHALFOUNE H. IRC 2013, 20-22 March 2013, Paris, France, Paper 54

[75] HUY MAI Le, & GIESE U. IRC, 20-22 March 2013, Paris, France, Paper 74

[76] HEPBURN C. Rubber Compounding Ingredients, Part 1, Rapra Review Report 79, 1994

[77] BLOW C.M., & HEPBURN C. *Rubber Technology and Manufacture*. Butterworth Scientific, Second Edition, 1982

[78] BRYDSON J.A. *Rubbery Materials and Their Compounds*. Elsevier Scientific, 1982

[79] MRPRA. The Natural Rubber Formulary and Property Index, 1984

[80] KLINGENDER R.C. *Handbook of Speciality Elastomers*. CRC Press, 2008

[81] DATTA R.N. *No 12*. . Rapra Technology Limited, **Vol. 12**, 2002

[82] EVANS M.S. *No 8*. . Rapra Technology Limited, **Vol. 12**, 2002

[83] BRYDSON J.A. *Rubber Chemistry*. Applied Science Publishers, 1979

[84] SIMPSON R.B. *Rubber Basics*. Rapra Technology Limited, 2002

[85] LONG H. *Basic Compounding and Processing of Rubber*. ACS Rubber Division, 1985

[86] WHITE J.R., & DE S.K. *Rubber Technologists Handbook*. Rapra Technology Limited, **Vol. 1 and 2**, 2001

[87] FORREST M.J., & WILLOUGHBY B.G. Overview of Rubber Breakdown Products, RubberChem, Birmingham 9th/10th Nov 2004

[88] FUNT J.F. *Mixing of Rubber*. Smithers Rapra Limited, 2009

[89] BHOWMICK A.K., & NIJMAN G. *Current Topics in Elastomer Research*. Boca Raton, 2008

[90] Malaysian Rubber Review: Production, Consumption and Market, Malaysian Rubber Review 12, No 3, 3rd Quarter 2009

[91] MAJUNDAR S. Rubber Vulcanization Processes: An Overview. *Chem. Week.* 2008 Aug 26th, **LIV** (2) pp. 211–218

[92] LEE M. An Overview of the High Performance Elastomers Market: High Performance & Speciality Elastomers 4th Int. Conference, Germany, 5/6th Dec. 2007, Paper 1

[93] CHAIEAR N., & SAEJIW N. *Update on Health and Safety in the Rubber Industries.* Smithers Rapra, 2010

[94] Summary Tables: Production, Consumption and Stocks of Natural and Synthetic Rubbers, *Rubber Statistical Bulletin 60*, No 4-5, Jan/Feb. 2008, p2-8

[95] Rubber Compounding Ingredients Sourcebook, 2000, Rapra Technology Limited

[96] DIN 75201, *Determination of the fogging characteristics of trim materials in the interior of automobiles*

[97] VDA 278, *Thermal Desorption Analysis of Organic Emissions for the Characterization of Non-Metallic Materials for Automobiles*

ICS 83.020

Price based on 52 pages