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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

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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

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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).

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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*.

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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.

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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.

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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.

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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]

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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]

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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]

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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]

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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]

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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.

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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]

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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

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