TECHNICAL REPORT



First edition 2017-02

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

utch. nées de . Norman and a second and a second a se *Caoutchouc* — *Examen exhaustif de la composition et de la nature des*



Reference number ISO/TR 21275:2017(E)



© ISO 2017, Published in Switzerland

All rights reserved. Unless otherwise specified, no part of this publication may be reproduced or utilized otherwise in any form or by any means, electronic or mechanical, including photocopying, or posting on the internet or an intranet, without prior written permission. Permission can be requested from either ISO at the address below or ISO's member body in the country of the requester.

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

Fore	eword		v		
Intr	oductio	n	vi		
1	Scop	e	1		
2	Norr	native references			
3	Tern	Ferms and definitions			
4 Overview of the rubber inductry					
•	4.1	General			
	4.2	Rubber component production processes	8		
	4.3	Generic rubber types	11		
	4.4	Rubber chemicals and additives	12		
	4.5	Mechanistic chemistry of rubber vulcanization	13		
		4.5.1 Generality	13		
		4.5.2 Sulfur-accelerated cure systems	13		
		4.5.3 Peroxide-based cure systems	14		
		4.5.4 Metal oxides	14		
		4.5.5 Other vulcanizing systems	14		
	4.6	Effect of elevated temperature on rubbery polymers and rubber additives	15		
5	Defi	nition of rubber fumes			
6	Natu	re and composition of rubber fumes	16		
U U	6.1	General			
	6.2	Key components of rubber fumes and their origin			
	6.3	Trapping and analysis of rubber fumes	17		
	0.0	6.3.1 General			
		6.3.2 Characterization studies carried out in factory environments	17		
		6.3.3 Characterization studies carried out under laboratory conditions			
	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	19		
		6.4.1 General	19		
		6.4.2 Overall trend in rubber workers' exposure to total rubber fumes	19		
		6.4.3 Polyaromatic hydrocarbons	19		
		6.4.4 Nitrosamines	19		
		6.4.5 Silane coupling agents and resorcinol steel cord coating agent	19		
7	Facto	ors affecting the variability of rubber fumes	19		
	7.1	General	19		
	7.2	Influence of the rubber compound formulation on the composition of rubber fumes	20		
	7.3	Influence of different manufacturing processes on rubber fumes	20		
	7.4	Influence of different processing temperatures on the composition of rubber fumes	21		
8	Revi	ew of literature on the composition and nature of rubber process fumes			
-	8.1	Comprehensive literature search	22		
		8.1.1 General	22		
		8.1.2 Rubber fumes data obtained from factory atmospheres	22		
		8.1.3 Rubber fumes data obtained by laboratory studies	32		
		8.1.4 Research on sampling and analysis techniques for rubber fumes			
		8.1.5 Influence of rubber additives on the composition of rubber fumes	38		
		8.1.6 Work carried out at Rapra Technology Ltd.	40		
	8.2	Other sources of information	41		
		8.2.1 General	41		
		8.2.2 Search strategy for external databases	42		
		8.2.3 Chemical abstracts results	42		
		8.2.4 General POLLUAB and NTSI database results	43		

	8.2.5	Search of industry-relevant publications, government publications and relevant websites	43
9	Summary of t	the finding of the literature review	44
10	Conclusions		45
Anne	x A (informative	e) Abbreviated terms	47
Bibli	ography	, 	49
jų	ograpny		±9
IV		© ISO 2017 – All rights reser	<i>v</i> ed

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 <u>www.iso.org/patents</u>).

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.

π tee ISL

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.

<u>Table 1</u> 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.

\mathbf{O} .	Table 1 — Range of Fubber 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, min- ing 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 fab- rics, 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, mem- branes 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

Table 1 — Range of rubber components

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.

ISO/TR 21275:2017(E)

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 <u>Annex A</u>.

<text> © ISO 2017 - All rights reserved

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 <u>http://www.electropedia.org/</u>
- 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]