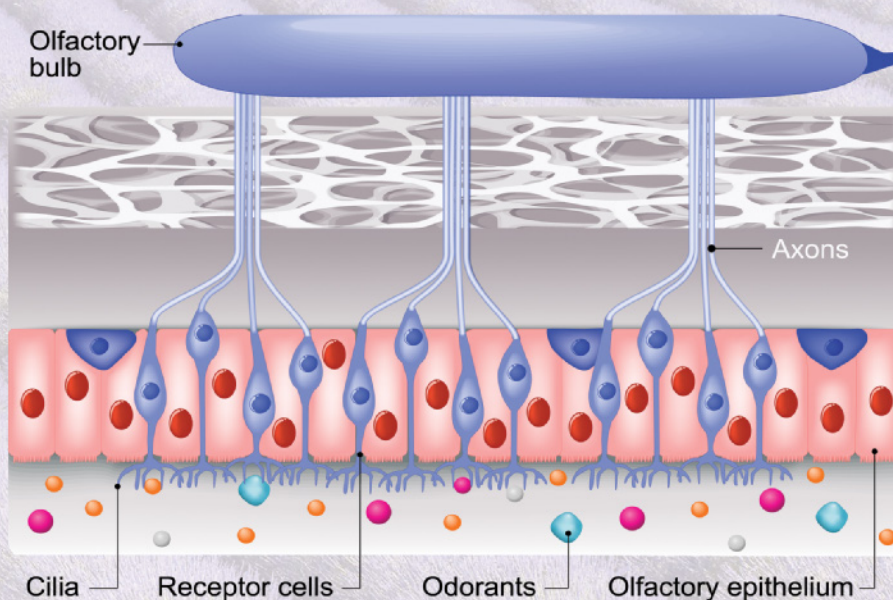


2ND Edition

Handbook of Odors in Plastic Materials

George Wypych



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Second Edition

George Wypych



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INTRODUCTION

Olfaction is one of the senses – smell. Olfaction or the sense of smell can recognize the smell of different odorants. Each chemical substance is a different odorant, which can be recognized by the sense of smell at a particular concentration. Sensitivity of olfaction for the different odorants varies, which makes the usefulness of smell a complex matter in recognition of the danger of the presence of different chemicals in our surroundings. Some chemical compounds can be recognized by the sense of smell at very low concentrations (0.00000001 mg/l). On the one hand, smell is a very powerful early warning system, but on the other hand the extensive smell of a chemical compound does not necessarily mean that the chemical compound is present at a high or a dangerous concentration.

At the same time, intensity of smell is a characteristic feature of a chemical substance and its presence affects the olfactory response of a material into which the chemical compound is incorporated.

Most products are meant to have no smell. There are exceptions, such as fragrances, flowers, or cosmetics, in which the composition of volatile odorants (scents or aromas) is very essential to their appeal, but in most cases products should have no odor.

Product and processing technology are typically concerned about the selection of the best composition of materials which can be easily processed to form a product having the best possible properties to satisfy user needs. Odor formation is the result of composition or may be caused by processing or other external factors, discussed below. In most technological processes, odor is not a factor to be considered unless there are complaints from users.

Such an approach is no longer acceptable in industry, which needs to compete for the best position to sell products which satisfy all potential expectations and are relatively inexpensive. This makes studies of olfactory perception very important in modern technology. This can be found from the extensive patent literature, and its study shows that most questions about product smell are being answered during the last decade, which have witnessed ever increasing interest in these investigations. It is quite well known from Mercedes-Benz that it employs a special group of people who are responsible for analysis of all products used in their cars that may affect the sense of smell of users. It was also known for a long time that new cars smell differently, and that this smell is caused by various chemicals used in the production of vehicles. These smelling chemicals are not appreciated any longer since indoor pollution is also considered in small spaces such as car interiors and they are implicated in potential danger to the health of occupants.

The major aim of this book is to analyze all factors responsible for the odor of products, which permit definition of problems related to a particular product, outline potential

dangers of problems with odor for different polymeric materials and groups of products, outline methods of analysis, and methods of elimination of odors.

This is the first book ever written on this important subject and it discusses details of odor in plastic materials in 14 chapters.

Mechanisms of odor formation and transport of odor-causing components within a material until they appear on its surface, where they can effectively evaporate, is the subject of chapter 2. This chapter discusses the presence of volatile chemicals, biodegradation, effect of temperature, oxidation, light exposure, and γ -irradiation on the odor of different products. Also, effect of the composition of different odorants is considered as it influences the overall odor of the product. Migration, leaching, and partitioning are considered in the transportation of odors inside the product.

Different odorants and their compositions produce distinctive, characteristic odors, which are discussed in chapter 3. Odors are classified according to six fundamental sensations, such as spicy, fruity, resinous, foul and burnt. In plastic materials, 14 distinctive odors were identified by testing panels, and they are discussed in detail.

Taste and smell are separate sensory systems in humans and animals. Taste is frequently defined by similar distinctive features as odors. The effect of various components on the taste of plastic materials is discussed in chapter 4.

Fogging is a physical property of a chemical compound being part of a more complex system, usually plastic material. Although fogging does not necessarily mean that a substance has smell, it is frequently the case as learned from the experiences of the automotive industry. Information about fogging in plastic materials is included in chapter 5.

There are many reasons for odor formation in plastic materials; some are discussed in chapter 2. In chapter 6, the effects of polymer, additives, processing conditions, recycling, contact with other materials, storage conditions, and humidity are discussed.

Methods of testing in the odor analysis are very important in understanding the reasons for odor formation in products. Products are usually manufactured from a mixture of many raw materials. In some products, 30 or more raw materials may be used to produce final goods, which perform in practical conditions. Each of these raw materials can be a mixture or contain a number of volatile materials. The discussion of the subject begins with analysis of the mechanism of smell and sampling. Several methods are in frequent use in industry and research, and these include active odor sensing, electronic nose, sensory analysis, gas chromatography/mass spectroscopy, combination of gas chromatography and olfactometry, and threshold odor number. All these methods are discussed in chapter 7, in addition to discussion of sensors and visualization.

Different polymers have different sensitivity and different reasons for affecting our sense of smell. The 39 polymers are discussed in chapter 8 in available detail in respect to odor and its origins.

Similar is the situation of different product groups. Products are complex mixtures of many different chemical compounds and their smell may result from different external actions related to their production methods and conditions of use. The 42 groups of different product are discussed in chapter 9 to outline known factors affecting the odor of these different products.

Some processing methods include operations which contribute to the specific influence on product odor. Chapter 10 considers 10 different processing methods from the

point of view of their effects on the odor of the final product, reasons for its formation, and methods of its prevention.

Eighteen different methods were developed to remove odor from products and materials. These include chemical methods, such as ozonation, oxidation, microoxygenation, complex formation, photocatalysis, and stabilization; physical methods, such as coagulation, degassification, absents, activated carbon and other adsorbents, filtration, and scavengers; biological methods, such as biodegradation, microorganisms enzyme, and biofiltration; and other methods including odor-masking and odor-stripping. All these methods are discussed in chapter 11.

The last three chapters discuss regulations, health and safety, and indoor air quality to give a comprehensive review of the subject.

The information in this book is based on published research papers and patented inventions. The subject is new, therefore there are numerous gaps in knowledge and understanding, but the subject is very important for modern industry, which needs to consider all aspects of consumer appeal, and odor is one very essential characteristic because it strongly affects one of our senses. Customers may not understand the scientific reasons behind the product odor, but their decision to buy the product will be certainly affected by using their own sense of smell.

From the linguistic point of view, compared to the other senses, smell is linguistically challenged.¹ Each sensory domain has its own lexical field: a set of words codifying the distinctions in that modality.¹ Smell stands apart.¹ When English speakers name smells they typically refer to its source (e.g., “it smells like banana”).¹

The predominant special senses in man are vision and hearing, olfaction occupying a quite unimportant position in the scale.² Smell and taste are usually regarded as allied senses.²

The above two citations show that the inferior development of knowledge on smells and odors has deep roots in language and perception. Our present sense of hygiene is also not very old from a historical perspective, considering that it was rapidly developed in the last century and was not such a high priority even a few centuries ago. On the other hand, connection of smells and odors with wellbeing is today a very strong driving force behind the current studies and makes this discipline to become a very essential part of culture and scientific development.

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- 2 McKenzie, D, *Aromatics and the Soul. A Study of Smells*, Elsevier, 2013, pp. 43-58.

MECHANISMS OF ODOR FORMATION AND ITS TRANSPORT

2.1 VOLATILE CHEMICALS

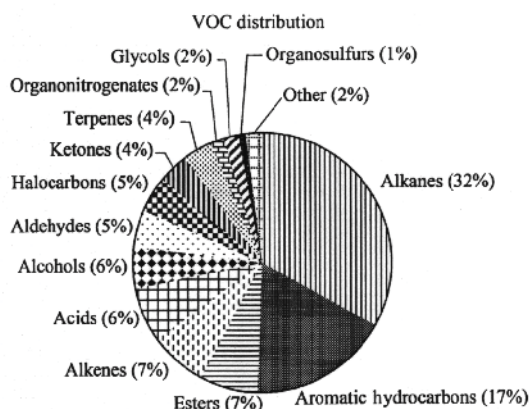


Figure 2.1. Percentage of compounds by family identified in building environment. [Adapted, by permission, from Gallego E, Roca X, Perales J F, Guardino X, *J. Environ. Sci.*, **21**, 333-39, 2009.

Figure 2.1 and the chemical breakdown of the composition of each family is given in Table 2.1.

Table 2.1. The most common VOC components as members of different chemical families. [Data from Gallego E, Roca X, Perales J F, Guardino X, *J. Environ. Sci.*, **21**, 333-39, 2009.]

VOC components by their chemical families
Alkanes n-Hexane, n-heptane, n-octane, n-nonane, n-decane, n-undecane, n-dodecane, 2-methylpentane, 3-methylpentane, n-tridecane, n-tetradecane, n-pentadecane, n-hexadecane, cyclohexane, methylcyclohexane
Alcohols Ethanol, isopropanol, 1-butanol, 3-ethyl-1-hexanol

The most indoor air pollution comes from sources inside the building, such as adhesives, carpeting, wood products, cleaning products, and many others, which may emit volatile organic compounds, VOCs.¹ The outdoor air that enters the building can also be the main source of indoor air VOC pollution.¹ The VOC indoor concentrations relate to the sick building syndrome, which affects the well being of its inhabitants.

One hundred and thirteen VOC compounds have been identified in an office environment.¹ Their distribution by chemical family contribution is given by

Table 2.1. The most common VOC components as members of different chemical families. [Data from Gallego E, Roca X, Perales J F, Guardino X, *J. Environ. Sci.*, **21**, 333-39, 2009.]

VOC components by their chemical families
Glycols 2-Methoxyethanol, 1-methoxy-2-propanol, 2-ethoxyethanol, 2-butoxyethanol, 2-butoxyethoxyethanol
Aldehydes Butanal, pentanal, hexanal, heptanal, n-nonanal, decanal, benzaldehyde, formaldehyde
Ketones Acetone, methylethylketone, cyclohexanone, methylisobutylketone, acetophenone
Halocarbons Dichloromethane, chloroform, trichloroethylene, tetrachloroethylene, p-dichlorobenzene, trichloronitromethane, 1,1,1-trichloroethane
Esters Methyl acetate, ethyl acetate, butyl acetate, iso-propylacetate, 2-ethoxyethyl acetate, texanol isobutyrate
Aromatic hydrocarbons Benzene, toluene, ethylbenzene, m+p-xylene, styrene, 1,2,4-trimethylbenzene, m-ethyltoluene, 1,3,5-trimethylbenzene, n-propylbenzene, naphthalene, tetrahydrofuran, 2-pentylfuran, o-ethyltoluene, p-ethyltoluene
Acids Acetic acid, pentanoic acid, hexanoic acid, octanoic acid
Terpenes α -Pinene, DL-limonene, β -pinene, 3-carene
Amides N,N-Dimethylformamide
Organosulfurs Carbon disulfide
Organonitrogenates Acetonitrile

At Qatargas, approximately 32,000 VOC components are in continuous surveillance as part of a robust fugitive emission Leak Detection and Repair program.² This program reduces fugitive emissions by 97% since its full implementation. It is an important undertaking designed to reduce contribution to the atmospheric photochemical reactions leading to the formation of ground level ozone.²

Odor intensity of a particular chemical compound is measured by the odor threshold, which is a characteristic property of a chemical compound. Table 2.2 gives the odor thresholds of some aldehydes.

Table 2.2. Contribution of aldehydes to the sensed odor. [Data from Hyttinen M, Pasanen P, Bjoerkroth M, Kalliokoski P, *Atm. Environ.*, **41**, 4029-39, 2007.]

Aldehyde	Odor threshold, $\mu\text{g m}^{-3}$
Formaldehyde	1072
Acetaldehyde	339
Propanal	65
Butanal	28
Benzaldehyde	186
Pentanal	22
Hexanal	58
Heptanal	23
Octanal	7.2
Nonanal	13.4
<i>trans</i> -Nonenal	0.14
Decanal	5.9

The lower the value of the odor threshold, the more intense the smell. It is quite apparent that the *trans*-nonenal has an exceptionally low value of odor threshold. Also, nonanal and decanal have low values of the odor threshold.

An uncomfortable smell was reported by employees of a medical center when the office was refurbished.⁴ Odor air quality was studied in the complaint area to identify possible sources of smell. The more intensive odor was found in the area where high VOC concentrations were also detected.⁴ Nonanal and decanal concentrations were correlated to the uncomfortable smell. These long-chain aldehydes are formed during the oxidation degradations of fatty acids, such as linoleic acid, linoleic acid and oleic acid, which are ingredients for many building products, including linoleum and surface coatings.⁴ Laser printers emit ozone, which contributes to degradation of linoleum and surface coatings.⁴ The problem of the uncomfortable smell was mitigated by use of a more effective ventilation flow rate, which reduced the concentration of odorous chemicals to below their odor threshold levels.⁴

VOC indoor concentration was related to the sick building syndrome.¹ Mild neutropenia was observed in one of the inhabitants with absolute neutrophil counts ranging from 1306 to 1319 cells/mm³.¹ Before occupants started the complaints, the absolute neutrophil count was 2540 cells/mm³ for this inhabitant.¹ Neutropenia is a decrease in circulating neutrophils in the peripheral blood, and abnormal absolute neutrophil count values are below 1500 cells/mm³.¹ The neutropenia can be caused by exposure to drugs and chemicals, such as industrial solvents.¹

In ventilation systems, supply air filters are usually the main source of odor, but also dirty ventilation ducts, heating coils, and heat exchangers may emit odors.³ Aldehydes,

carboxylic acids, and nitrogen-containing organic compounds were the main emission products in the thermodesorption analyses of the filter dust.³ Many of these compounds have low odor threshold values and, therefore, contribute to the odor released from the filters.³ Elevated temperature, presence of ozone, and elevated humidity assist desorption of odorous substances from filters.³ Decanal and nonanal were also found in this case to be the most persistent odorants.³

Employees complained about eye irritations, sore throats, and unspecific symptoms after moving to a new building.⁵ Overall concentration of VOC in this building were relatively low.⁵ But high concentrations (4300–7800 mg/kg) of tris-(2-butoxyethyl)-phosphate, TBEP, and diethylhexylphthalate, DEHP, (980–3000 mg/kg) were found in dust samples.⁵ The coating of the rubber floor was identified as the source of TBEP, while no single predominant source of DEHP was found.⁵ After removal of the coating of the rubber floor throughout the whole building, a reduction up to 90% of TBEP in the dust samples was found.⁵ This action was essential to reduce complaints.

A body weight of a person influences gustatory and olfactory perception in healthy adults.⁶ Increasing body mass index, BMI, is associated with a decrease in olfactory and taste sensitivity.⁶

There is increasing pressure from regulations to reduce VOC in waterborne coatings and formulate low odor coatings.⁷ To achieve this goal, coalescing aids are being taken out of the formulations.⁷ Considering that film-forming properties need to remain identical, binder polymers that exhibit low minimum film formation temperatures are being developed and utilized for formulating coating with the expectation that the resulting products exhibit the same, if not better, performance as the traditional ones containing significant amounts of solvents.⁷

Three different pipes (HDPE, PEX, and PVC) for drinking water were tested with respect to migration of volatile organic components (VOC) to water.⁸ The odor of water in contact with plastic pipes was assessed according to the quantitative threshold odor number.⁸ A major migrating component from HDPE pipes was 2,4-di-*tert*-butyl-phenol, which is a known degradation product from antioxidants such as Irgafos 168s.⁷ In addition, a range of esters, aldehydes, ketones, aromatic hydrocarbons and terpenoids were identified as migration products from HDPE pipes.⁸ Threshold odor number values larger than 4 were determined for five out of seven brands of HDPE pipes.⁸ PEX pipes had also high threshold odor number and odor was detected in water samples.⁸ Migration tests of PVC pipes revealed few volatile migrants in the test samples and no significant odor of the test water.⁸

2.2 BIODEGRADATION

Biodegradation and biodeterioration of various products are topic by themselves – too broad to discuss it in full detail. The special monographic source is available, which contains detailed information on the subject of biodegradation and biodeterioration of different materials.⁹ Biodegradative processes act in two directions: they spoil materials, frequently producing unpleasant odors, and they help to remediate existing odors formed in materials (see chapter 11).

The most common case of spoilage is related to food products, which are affected by the action of microorganisms in a matter of hours, depending on temperature, relative

humidity, and availability of microorganisms. Some of the most common food borne pathogens include *Escherichia coli*, *Salmonella spp.*, *Bacillus cereus*, and *Vibrio parahaemolyticus*.¹⁰ Some pathogens do not produce any odor or do not change taste, but they produce toxins harmful for humans and animals. Odor producing microorganisms have enzymes which are able to biodegrade foods to smaller molecules, which are volatile and they produce odors at small concentrations. This includes microorganisms containing lipases, which are enzymes able to digest lipids and fats with the production of fatty acids – some of which produce odors. Bacteria-producing sulfides are another common example of microorganisms which produce strong odor. Odors are not only produced as a result of food spoilage, but also result as a side effect of the production of food. Rotten egg odor of hydrogen sulfide is responsible for most of the odor problems associated with the brewery and food processing wastewater treatment. Heavier than air, colorless, corrosive and extremely toxic, its presence raises serious workplace health and safety concerns.

Another common case of odor-producing bacteria is the one that causes body odors. These bacteria are present on the skin. Typical examples of these odor producing bacteria include *Bacillus subtilis*, *Corynebacterium xerosis*, and *Staphylococcus epidermidis*.

Microorganisms producing odors, similar to any other microorganism, cause biodegradation and biodegradation to obtain nutrients necessary for their life and growth. It is thus pertinent that material of plant or animal origin will likely be preferable source of biodeterioration. Skins of animals used by the leather industry are one good example. Soaking is one of the operations in leather industry. During this operation, proteolytic enzymes digest proteins and cause formation of unpleasant smell.⁹ Also, long transportation or storage of raw skins causes biodegradation producing odors.

Many industrial products are also biodegraded with the formation of odor producing compounds. Paints and coatings are attacked by *Escherichia*, *Enterobacter*, *Klebsiella*, *proteus*, and *Pseudomonas*, which results in production of odors. Numerous species of bacteria and fungi can digest wool with the formation of odors.

Fuels have to be protected from the action of microorganisms because their action may contribute to serious breakdowns in aerospace and automotive equipment and maintenance problems, lesser known is that bacteria produce toxic hydrogen sulfide in fuel storage tanks.⁹ Also, heating oil is used by microorganisms with production of unpleasant odors.

Pseudomonas, filamentous fungi, such as *Aspergillus fumigatus*, and yeast use lubricants with production of characteristic odors. Rancid fat odors are volatile metabolites of aerobic bacteria and hydrogen sulfide produced from biodegradation of oil-water emulsions used in coal mines.

Microorganisms such as fungi and bacteria (i.e. *Cladosporium* sp. and *Pseudomonas* sp.) biodeteriorate cellulose, which is the main component of natural fibers such as flax and cotton, causing odor emissions.¹¹

Film archivists know that the serious decomposition of cellulose-triacetate-based cinematographic film is accompanied by the loss of acetic acid.¹² When the film container is opened the release of acetic acid is immediately noticeable.¹² Its characteristic odor accounts for what is known as the “vinegar syndrome.”¹²

The above are just the most common or unusual examples, because biodegradative changes producing volatile substances causing odors are common.

It should be mentioned that biocides used for the protection of common products may also contribute to the odors. These include the following groups of biocides: acetal aldehyde-releasing compounds, acid esters, acids, active halogen products, aldehydes, carbamates, formaldehyde-releasing compounds, and phenolics.

2.3 EFFECT OF TEMPERATURE AND TIME

Elevated temperature may cause degradation of material and evaporation of its components. Table 2.3 shows examples of degradation products for some polymers.¹³

Table 2.3. Thermal degradation products of some polymers. [Data from Hakkarainen M, *Adv. Polym. Sci.*, **211**, 23-50, 2008.]

Polymer	Thermal degradation products
Polyamide 66	Cyclopentanones, pyridines, cyclic imides, amides, carboxylic acids, caprolactam
Polyethylene	Ketones, carboxylic acids, furanones, ketoacids
Poly(ethylene oxide propylene oxide-ethylene oxide)	Formates, acetates, carboxylic acids, aldehydes
Poly(L-lactide)	Lactide, lactic acid, lactoyl lactate
Poly(methyl methacrylate)	Methyl methacrylate
Polysiloxane rubber	Cyclic oligomers
Polystyrene	Styrene, styrene acrylonitrile, t-butylbenzene, α -methylstyrene, butylated hydroxytoluene
Polysulfide	1,3,6,7-dioxadithionane, other cyclic products

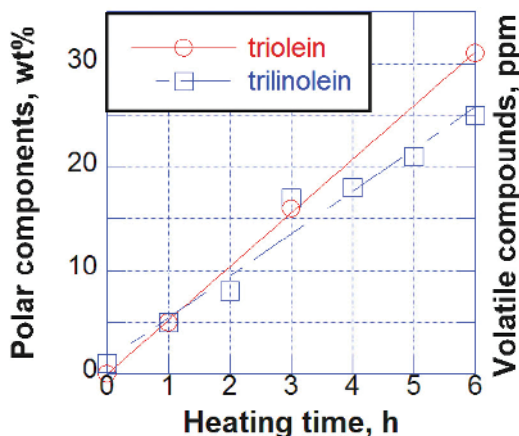


Figure 2.2. Formation of polar compounds in heated oil systems vs. heating time at 190°C. [Data from Neff W E, Warner K, Byrdwell W C, *JAOCs*, **77**, 12, 1303-14, 2000.]

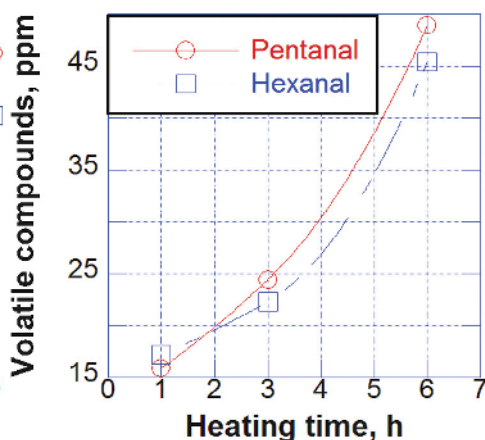


Figure 2.3. Emission of some volatile compounds from triolein vs. heating time at 190°C. [Data from Neff W E, Warner K, Byrdwell W C, *JAOCs*, **77**, 12, 1303-14, 2000.]

In order to better understand production of undesirable odors, such as fruity, plastic, and waxy that are characteristic of higher oleic acid-containing oils, model heated oil sys-

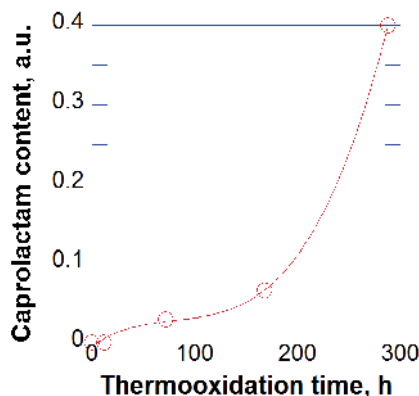


Figure 2.4. Caprolactam content in emitted volatiles vs. thermooxidation time at 90°C. [Data from Hoeglund A, Lindqvist A, Albertsson A-C, Berglund B, *Polym. Deg. Stab.*, **97**, 481-87, 2012.]

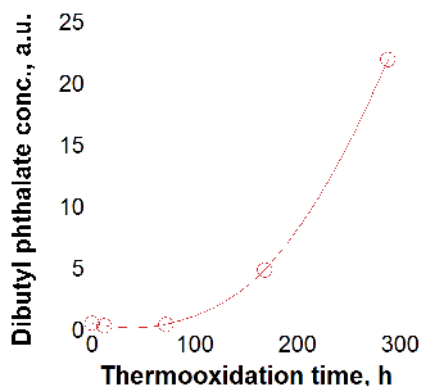


Figure 2.5. Dibutyl phthalate content in emitted volatiles vs. aging time at 90°C. [Data from Hoeglund A, Lindqvist A, Albertsson A-C, Berglund B, *Polym. Deg. Stab.*, **97**, 481-87, 2012.]

tems of triolein and trilinolein were studied.¹⁴ The predominant odors of the triolein heated 1, 3, and 6 h at 190°C were fruity and plastic, in combination with other odor types, such as acrid and grassy.¹⁴ Figure 2.2 shows the effect of heating time on the formation of polar compounds as a result of oxidation during heating.¹⁴ Figure 2.3 shows the effect of heating time on emission of some volatile compounds.¹⁴

The aldehydes were produced by the thermal decomposition *via* homolytic cleavage of the oxidation functional group atoms (hydroperoxy, keto, epoxide, and dimer oxygen linkages).¹⁴ By an acid heterolytic cleavage between an adjacent double bond and a carbon bearing a hydroperoxy group or by the action of both homolytic and heterolytic decomposition mechanisms (mixed mechanism), these aldehydes can be produced from hydroperoxy products under the conditions of heating.¹⁴

Polyamide 66 was subjected to accelerated ageing through thermooxidation at 100°C.¹⁵ After different degradation times, participants of the testing panel smelled jars with aged polymer and recorded their perceived odor intensity according to a scale.¹⁵ Also, conventional analyses by GC/MS and tensile testing were performed to measure the volatile compounds released and changes in the mechanical properties during degradation.¹⁵ Odor intensity correlated with a significant deterioration in mechanical properties and the release profiles of eight degradation products.¹⁵ Some compounds emitted were the result of thermal degradation and some were a result of evaporation. Figure 2.4 shows the effect of thermodegradation time on the formation of caprolactam (degradation) and Figure 2.5 shows the effect of thermodegradation time on the evaporation of plasticizer (dibutyl phthalate).¹⁵ It is pertinent that plasticizer evaporation was more rapid than polyamide degradation.¹⁵

Different deodorization temperatures were used to deodorize fish oil.¹⁶ Because of the occurrence of numerous methylene-interrupted ethylenic double bonds, polyunsaturated fatty acids, such as eicosapentanoic, EPA, and docosahexanoic, DHA, acids are very sensitive to oxygen presence and temperature.¹⁶ Figure 2.6 shows that with increased temperature the concentration of polyunsaturated acids dramatically decreases.¹⁶ These fatty

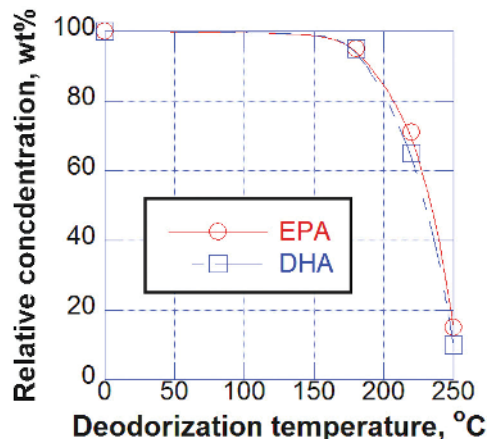


Figure 2.6. Relative concentration of polyunsaturated fatty acids vs. deodorization temperature. [Data from Fournier V, Destailats F, Juaneda P, Dionisi F, Lambelet P, Sebedio J-L, Berdeaux O, *Eur. J. Lipid Sci. Technol.*, **108**, 33-42, 2006.]

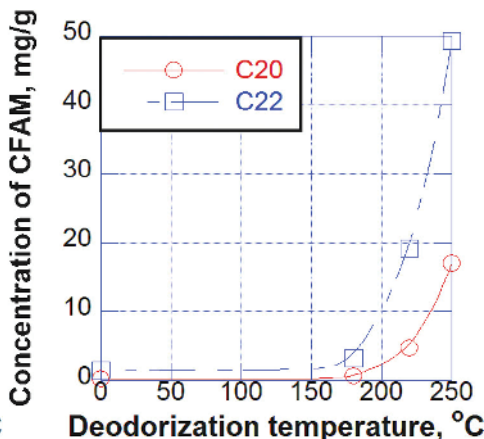


Figure 2.7. Concentration of cyclic fatty acids derived from C20 and C22 unsaturated fatty acid during deodorization of fish oil. [Data from Fournier V, Destailats F, Juaneda P, Dionisi F, Lambelet P, Sebedio J-L, Berdeaux O, *Eur. J. Lipid Sci. Technol.*, **108**, 33-42, 2006.]

acids are essential nutrients for the central nervous system.¹⁶ Various degradation products are formed, including polymers, cyclic fatty acids, and geometrical isomers of EPA and DHA. Figure 2.7 shows the kinetics of formation of cyclic fatty acids, CFAM.¹⁶

2.4 EFFECT OF LIGHT EXPOSURE

Sour cream packaged in cups having different light barrier properties (white, medium light barrier, and high light barrier) was exposed for 36 h to the radiation of a standard fluorescent bulb.¹⁷ This amount of radiation was simulating storage conditions in Norwegian grocery stores.¹⁷ The quality of sour cream was evaluated by sensory analysis and fluorescent spectroscopy. Fluorescent emission spectra were measured in the range of 410 to 750 nm with excitation at 382 nm.¹⁷ This excitation wavelength had been shown earlier to give good results with regard to lipid oxidation in dairy products.¹⁷ The fluorescence measurements corresponded with the results of sensory analysis as the photosensitizers were degraded more when less protection was given by the cup.¹⁷ Figure 2.8 shows the intensity of off-odors in the sour cream as measured by sensory analysis (1 = lowest intensity, 9 = highest intensity).¹⁷

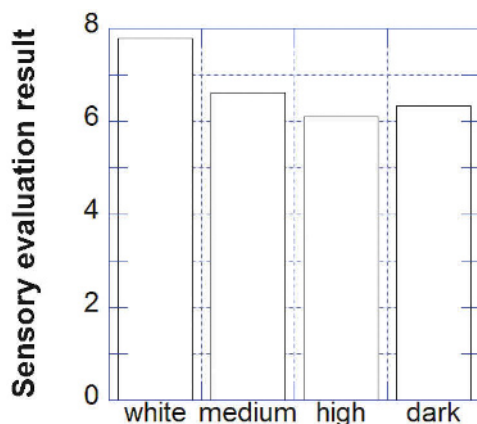


Figure 2.8. Sensory evaluation result of sour cream packaged in different materials (see text for explanations of conditions of experiment). [Data from Larsen H, Geiner Tellefsen S B, Veberg Dahl A, *J. Food Sci.*, **74**, 8, S345-S350, 2009.]

The sample denoted as “dark” was stored under the same conditions, but without radiation in a dark place.¹⁷ It is evident from

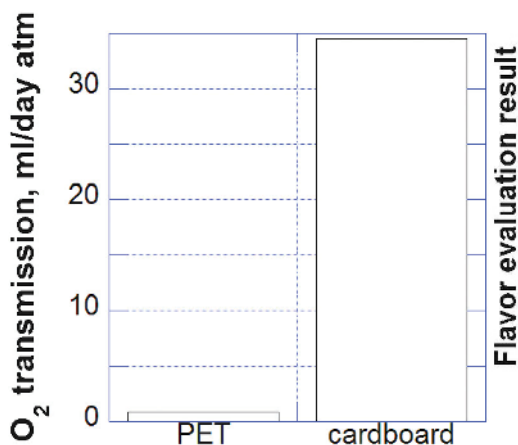


Figure 2.9. Oxygen transmission through PET and cardboard packaging materials for milk. [Data from Papachristou C, Badeka A, Chouliara I, Kondyli E, Kourtis L, Kontominas M G, *Eur. Food Res. Technol.*, **224**, 237-47, 2006.]

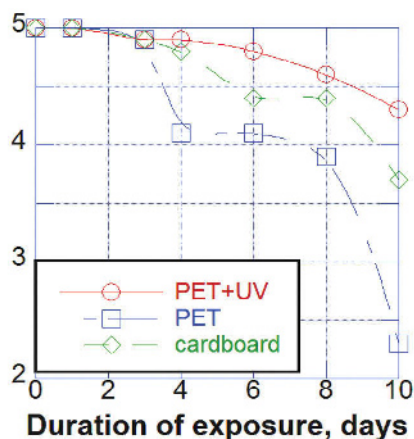


Figure 2.10. Flavor of milk change vs. duration of exposure to oxygen transmission as in Figure 2.9 and fluorescent radiation. [Data from Papachristou C, Badeka A, Chouliara I, Kondyli E, Kourtis L, Kontominas M G, *Eur. Food Res. Technol.*, **224**, 237-47, 2006.]

these results that radiation has prevailing effect on degradation of properties of sour cream, and the quality of protection has a strong influence on the quality of the product. The best protection was given by the cup denoted here as “high light barrier”. This cup was made from polystyrene having a total thickness of 300 μm and three layers: top containing TiO_2 , middle containing Al_2O_3 +carbon black, and bottom containing TiO_2 .¹⁷

Chemical, microbiological and sensorial changes in the premium quality, whole pasteurized milk stored at 4°C under fluorescent light was studied for a period of 13 days.¹⁸ Milk containers tested included 1 l bottles made of (a) clear 350-400 μm PET + UV blocker with a transparent label, (b) clear 350-400 μm PET + UV blocker with a white colored label, (c) clear 350-400 μm PET, and 1 l coated paperboard cartons stored under the same experimental conditions as the “commercial control” sample.¹⁸ Figure 2.9 shows that the transmission rate of oxygen through PET is much smaller than through cardboard.¹⁸ Figure 2.10 compares flavor changes vs. days of exposure to both oxygen and fluorescent lamp radiation.¹⁸ It is again evident that UV radiation has a dominant role in changing the properties of milk. It is also pertinent that application of UV stabilizer helps to preserve the original properties of milk, which are better because UV stabilizers reduce UV penetration and PET has much better barrier properties to oxygen than cardboard.¹⁸

Similar studies are reported in another paper, with the exception of multilayer HDPE pigmented with TiO_2 , multilayer HDPE pigmented with carbon black, and monolayer HDPE pigmented with TiO_2 , which were compared to clear PET, PET pigmented with TiO_2 , and milk packaged in commercial cardboard.¹⁹ Vitamin A losses recorded were 11% for multilayer and monolayer pigmented HDPE and pigmented PET bottles vs. 16% for the paperboard cartons and 31% for the clear PET bottles after 7 days of storage.¹⁹ Based on sensory analysis, the shelf life of low fat (15 g kg^{-1}) pasteurized milk is approximately

5 days.¹⁹ The best overall protection for the product was provided by the multilayer, followed by the monolayer TiO₂-pigmented HDPE bottle.¹⁹

Cheese was stored for up to 9 weeks under both fluorescent light and in the dark, packaged aerobically and under modified atmosphere packaging of (a) 100% CO₂, (b) 100% N₂ and (c) 50% CO₂/50% N₂.²⁰ Cheese samples stored under fluorescent light showed a higher degree of lipid oxidation (ca. 3–4 times higher for modified atmosphere packaging samples and 20 times higher for aerobically packaged samples) and suffered a gradual discoloration compared with samples stored in the dark.²⁰ Free fatty acids, esters, aldehydes, ketones, and alcohols were recorded for all treatments, with aerobic packaging and exposure to light, giving higher concentrations of volatile compounds compared with other treatments.²⁰ Sensory analysis showed that radiation, gas composition, and storage time significantly affected taste and odor attributes of grated Graviere cheese. The best sensory attributes were obtained using 100% N₂ or 50% N₂/50% CO₂ and storage in the dark.²⁰

A patent shows that in the photoinitiated frontal polymerization, a combination of photoinitiator(s) and thermal initiator(s) can be used in the system.²¹ Polymerization starts at the top layer as a result photoinitiation.²¹ The heat generated from photopolymerization causes thermal decomposition of thermal initiators, producing initiating radicals that initiate the polymerization; the polymerization front travels downwards from the surface to achieve a complete cure.²¹ Similar to the conventional thermal frontal polymerization, the amount of heat produced is essential in increasing the temperature of the immediate, uncured layer to the decomposition temperature of thermal initiators and to maintain the traveling front.²¹ It is possible to cure materials having a thickness of 1 cm or more.²¹ It is typically assumed that photoreactions are a surface phenomena but this example shows that with the right combination of components bulk changes can also be expected. With the complex materials used today, this effect can be inadvertently created to cause extensive changes in materials.

Cellulose diacetate degraded under UVA radiation did not show any significant sign of deterioration, while its samples degraded under UVB and UVC radiations were discolored and released vinegar odor.²²

2.5 EFFECT OF GAMMA-IRRADIATION

Sterilization of plastic packaging materials for food, pharmaceutical or cosmetic products with ⁶⁰Co γ -irradiation in the presence of oxygen can result in the formation of volatile substances. In the case of polypropylene, 3-ethylphenol and 3-propylphenol were generated by γ -irradiation (dose 20 kGy) with the highest rate.²³ Several volatile compounds present in PP packaging were degraded by γ -irradiation, including nonanal, hexanal, ethyl vaniline, octanal, (E)-non-2-enal, oct-1-en-3-one, and (Z)-non-2-enal.²³

Several plastic packaging were subjected to γ -irradiation.²⁴ Table 2.4 shows the effect of dose on different packaging materials.²⁴

Table 2.4. Effect of γ -irradiation on odor development in different packaging materials. [Data from Goulas A E, Riganakos K A, Kontominas M G, *Radiat. Phys. Chem.*, **69**, 411-17, 2004.]

Packaging material	Dose, kGy			
	5	10	30	60
Polystyrene				+
Polypropylene			+	+
Poly(ethylene terephthalate)				+
High density polyethylene		+	+	+
PVC/HDPE	+	+	+	+
HDPE/PA				+

+ indicates detectable difference between irradiated and reference sample (0 kGy)

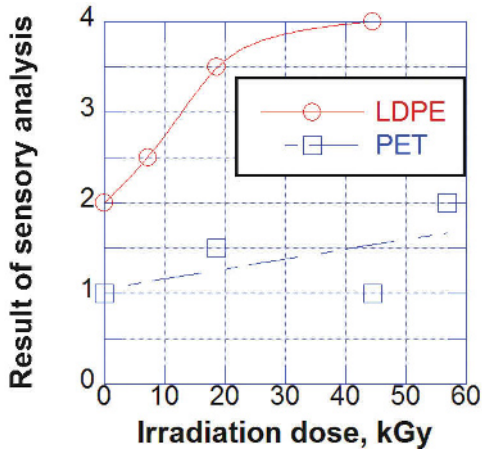


Figure 2.11. Effect of radiation dose on odor formation in LDPE and PET. [Data from Welle F, Mauer A, Franz R, *Radiat. Phys. Chem.*, **63**, 841-44, 2002.

Doses of 5 and 10 kGy are food approved irradiation doses; a dose of 30 kGy is a sterilization dose; and a dose of 60 kGy is a special purpose sterilization dose.²⁴ The overall migration values from sheet or bottle samples were significantly lower than the overall migration limit (10 mg/dm²) set by the EU for food grade plastic packaging materials.²⁴

Irradiation of packaging materials led to a formation of free radicals and ions, followed by crosslinking and oxidative chain scission.²⁵ These chemical reactions also result in a formation of volatile radiolysis products, which may cause off-odors in polymers and may change the migration characteristics of packaging materials.²⁵

Irradiation affects also polymer additives,

which change the specific migration behavior of polymer additives and additive decomposition products.²⁵ Figure 2.11 shows results of irradiation of packaging samples on odor formation evaluated by sensory analysis.²⁵ LDPE is more affected by irradiation than polyester.²⁵

The radiolysis substances generated in packaging materials consist of volatile and low molecular weight compounds.²⁶ In hermetically closed packages these compounds originate production of off-odors and can be transferred to the contained foodstuffs.²⁶ The chromatographic profile and the odor of irradiated bags filled with nitrogen were completely different to those filled with air.²⁶

2.6 MIGRATION

Migration is defined as the diffusion of an additive from a plastic to other contacting material.²⁷ Several assumptions are made in discussion and testing of migration, including:²⁷

- diffusion coefficient is considered independent of concentration
- the surrounding medium is considered to have infinite volume
- boundary layer phenomena are ignored
- migration may involve more than one component of formulation
- counterdiffusion is a frequent phenomenon when the diffusing component is lost by extraction
- the process involves diffusion to the surface and sorption from the surface (both processes usually have different rates and any one of them may be a rate-controlling step)
- process of diffusion is well described by the second law of Fickian diffusion (see below)
- specimens are considered very thin plane sheets with migration occurring mainly through faces (negligible through edges)

Some of the above assumptions are correct and some are false or misleading.

Fick's second law of diffusion is given by the equation:

$$\frac{\partial c}{\partial t} = -D \frac{\partial^2 c}{\partial x^2} \quad [2.1]$$

where:

c	concentration of diffusant
t	time
x	depth of penetration.

In the majority of real situations the concentration gradient is not constant (as in Fick's first law) but changes with time. Unlike Fick's first law (steady-state diffusion), Fick's second law describes non-steady state diffusion. Solution of equation [2.1] which produces a graphic representation deviating from that of Fick's second law, is often called non-Fickian behavior.²⁷

Odor formation in materials in contact with plastic materials is caused either by migration of original components of packaging formulation or migration of compounds formed by degradation of polymer(s) or their additives.

Important to notice is that many packaged products have an original aroma, which should be preserved by selection of adequate packaging material.

Acetaldehyde is a common degradation product of poly(ethylene terephthalate) formed during the melt condensation reaction and melt processing of PET.¹³ Acetaldehyde migrates into food from PET packaging.¹³ Butylated hydroxytoluene is an antioxidant commonly utilized as an additive in food and in rubber and plastic products. Its migration from plastic packaging into the package's content has been shown.¹³ Bisphenol A is used as a raw material to make polycarbonate, epoxy adhesives and can coatings.¹³ Many foodstuff containers are made of these resins, including containers for oven and microwave cooking.¹³ Solid-phase microextraction in combination with GC-MS showed that 0.7–78.5 $\mu\text{g L}^{-1}$ of bisphenol A leached from plastic containers to water.¹³ Phthalates

are used in the food packaging industry as adhesives, offset printing inks and lacquers.¹³ They are also found to migrate into foods.¹³

A solid phase microextraction, using PDMS fiber, was developed to identify the odor causing compounds in a PVC-coated foil blister packaging used in the pharmaceutical industry.¹³ The source of the odor was traced to ethyl-2-mercaptoacetate, formed by the unanticipated reaction of a common residual solvent (ethanol) in a widely used pharmaceutical tablet excipient with low-level residual amounts of reactants or synthetic intermediates of PVC resin thermal stabilizing agent.¹³ Phthalates were detected in the intravenous solutions contained in plastic containers, phthalates were also detected in syrup, lotion and eye drops, and DEHP easily leached from polyvinyl chloride tubing.¹³ The low molecular weight compounds included degradation products from PCL-PC and epoxidized soya bean oil formed during sterilization and impurities remaining from synthesis, i.e., acetophenone, caprolactone, phenol, 6-hydroxyhexanoic acid, and hexadecanoic acid.¹³

2-Ethoxy-2-methylpropane, commonly called ETBE, was identified as a contributor to odors from the silane-crosslinked polyethylene pipe. Aqueous concentrations of ETBE in pipe leachate ranged from a low of 23 mg/L to above 100 mg/L. The concentrations decreased with increased flushing.²⁸ Panelists were able to smell ETBE at a concentration of 5 mg/L and assigned a rating of a weak odor.²⁸ Disinfectants did not have influence on the migration of odorants.²⁸

The 25 odorous compounds have been identified in 12 commercial adhesives used in multilayer packaging products used for food.²⁹ The 76% of these compounds migrated into a dry food simulant (Tenax).²⁹ Some of these substances were detected by sniffers with acetic acid, butyric acid and cyclohexanol with vinegar, cheese and camphor odors being the most abundant.²⁹

The emission of H₂S from landfills in the United States is an emergent problem because measured concentrations have potentially unsafe levels for on-site workers and they may cause a nuisance and potentially deleterious health impacts to surrounding communities.³⁰ H₂S migration into the atmosphere can be mitigated by reducing its diffusion or using alternative cover soils with a high H₂S adsorption coefficient.³⁰ Specially selected cover soils may reduce migration of H₂S.³⁰

2.7 LEACHING

Removal of materials by dissolving them from solids is called leaching. The chemical process industries use leaching but the process is usually called extraction, and organic solvents are often used.

Leaching is frequently observed in some industrial products, for example, paints and sealants. In paints the phenomenon is known as a streak staining, surfactant leaching, surfactant staining, exudation, or weeping. It occurs with some exterior latex paints when water soluble components of the paint are extracted and deposited in sufficient concentration on the surface. Soluble ingredients in paints include dispersants, surfactants, wetting agents, thickeners, and glycols. Some silicone sealants are prone to release some of their composition forming streaks on the surface of glass. These sealants are used in glazing or connecting panes of glass.

Pipe relining *via in situ* epoxy lining is used to remediate corroded plumbing or distribution systems.³¹ This investigation examined the effects on odor, total carbon formation, and disinfectant demand in water exposed to epoxy-lined copper pipes used for home plumbing.³¹ The study was conducted in accordance with the Utility Quick Test, a migration/leaching method for utilities to conduct sensory analysis of materials in contact with drinking water.³¹ Sensory data indicated that the epoxy liner leached compounds that contributed a “plastic/adhesive/putty” odor to drinking water.³¹ The odor was present in water exposed to the pipe material, and its intensity did not diminish during subsequent flushing and stagnation periods within the timeframe of the utility quick test.³¹ While significant odor occurred after 72 h of leaching, short-term laboratory tests demonstrated that the odor imparted was proportional to stagnation time and was not detectable after only 1 h of leaching.³¹

A study of odor-causing compounds was conducted for the leaching of polyvinyl-chloride pipe and its joints, primer and cement, into drinking water distribution systems.³² The leaching study of the PVC pipe with its joint solvents (primer and cement) concluded that the original solvent compounds, and their reaction products that formed during the bonding process in the PVC pipe, were a primary source of the glue/varnish odor.³²

Ammonia and odor emissions from pig farms and nitrogen leaching from outdoor pig production can be reduced by lowering protein contents of feeds (less than 160 g of crude protein/kg).³³ Some reductions in odor emissions can be achieved by management of the ventilation rate, but the most effective measures are to cover slurry stores and to inject slurry into soil.³³

2.8 PARTITIONING

Partitioning of odor substances can be considered for different systems, such as

- polymer-polymer
- polymer-liquid
- polymers-gas
- gas-liquid

Very limited literature exists on the partitioning of odor compounds in any of these systems. Polymer-polymer partitioning is relevant in the case of polymer blends and multilayer laminates. It has limited value in odor evaluation, which is more related to a polymer-liquid system.

Off-lattice Flory-Huggins-based approach of partitioning of bulky solutes between polymers and interacting liquids has been developed.³⁴ Diffusion coefficients, partition coefficients between polymer and hydrogen-bonding liquids are the fundamental quantities to assess the loss of plastics constituents. For polymers with a crystallinity, the excess chemical potentials are also required for calculations.³⁴ This contribution is focused on the development of a combination of decision tools and predictive approaches of the contamination of food products and drinking water by synthetic materials in contact.³⁴

In various disciplines, octanol/water partitioning coefficient is in popular use. The octanol-water partition coefficient, K_{ow} , is a measure of the equilibrium concentration of a compound between octanol and water that indicates the potential for partitioning into soil organic matter (i.e., a high K_{ow} indicates a compound which will preferentially partition into soil organic matter rather than water). K_{ow} is inversely related to the solubility of a

compound in water. $\text{Log}K_{\text{ow}}$ is used in models to estimate plant and soil invertebrate bio-accumulation factors. Although of limited application for odor release from plastic materials to surrounding liquids, popular octanol/water partition coefficients may give some indication of partition which can be expected in a polymer-liquid system.

$\text{Log}K_{\text{ow}}$ coefficients have found application in analysis of perfume components.³⁵ Enduring perfume ingredients have $\text{log}K_{\text{ow}}$ of about 3 or higher.³⁵

The initial removal of an odor molecule is governed by gas/liquid partitioning.³⁶ The partitioning is an equilibrium process in which odors in gas phase migrate into the liquid droplet (e.g., sprayed mist) to establish an equilibrium by the partitioning coefficient of the system.³⁶ This process can be described using Henry's Law, which defines an equilibrium constant as a ratio of the amount of gas dissolved in a given liquid and the partial pressure of that gas in the gas phase, as in the following equation:³⁶

$$K = \frac{p}{c} \quad [2.2]$$

where:

K	equilibrium constant, Henry's Law constant
p	partial pressure of odor component
c	concentration of odor in solution.

2.9 ODOR-RELEASING DEVICES

Odor-releasing devices that allow repeatable, remote, and reliable switching of odor flux could have a significant impact on the effectiveness of virtual reality.³⁷

The primary requirement for the development of a gas-release device for odor generation is an accurate control capability.³⁷ From this perspective, an ideal device for odor generation should safely contain a suitable quantity of odor-releasable solution, can release little or no odor in the "off" state, and be repeatedly switched to the "on" state

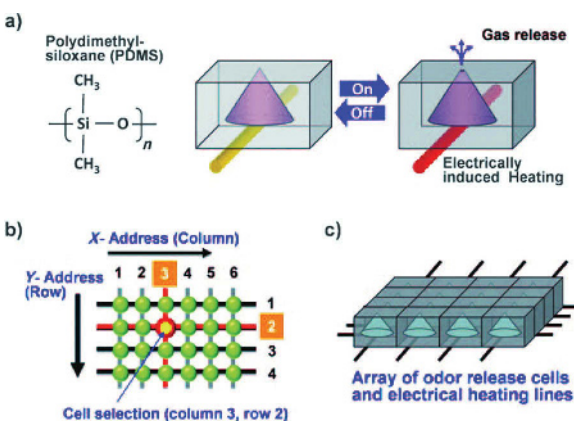


Figure 2.12. a) Proposed action of a gas/odor-release device based on an elastic chamber material. b) a diagram illustrating the x-y coordinate cell-selection method, and c) a X-Y matrix structured odor-releasing system with 4 x 4 cells. [Adapted, by permission, from Kim H, Park J, Noh K, Gardner C J, Kong S D, Kim J, Jin S, *Angew. Chem. Int. Ed.*, **50**, 6771-75, 2011.]

without mechanically disrupting the device.³⁷ Figure 2.12 shows the principle of action of a concept odor-releasing device. The proposed X-Y matrix of the odor-release system has an array of gas/odor containers with rows and columns of electrical heating lines, in which only the intersecting cell (and no other cells) from many arrayed cells is allowed to pass beyond the threshold accumulation of gas/odor pressure to force-open the cell gate for gas/odor release.³⁷ The size (volume) of a cone-shaped cell is 0.077 mL.³⁷ Each of the PDMS cells has a gate at the top made of a puncture hole

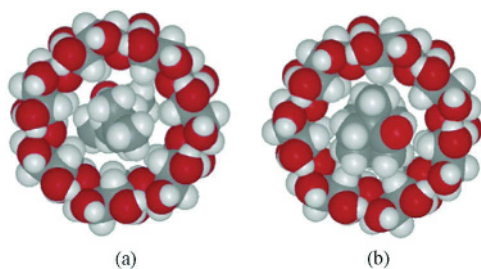


Figure 2.13. β -cyclodextrin complexes with linalool (a) and camphor (b). [Adapted, by permission, from Ciobanu A, Mallard I, Landy D, Brabie G, Nistor D, Fourmentin S, *Carbohydrate Polym.*, **87**, 1963-70, 2012.

stable 1:1 inclusion complexes are formed.³⁸ The most stable conformations which have been simulated are illustrated in Figure 2.13.³⁸ One can observe that both guest structures might be encapsulated in β -cyclodextrin, but that much more space remains free in the cavity in the case of linalool.²⁹ Thus, the influence of the steric complementarity probably explains the greater stability observed for camphor.³⁸

Fragrances are now increasingly being embedded in consumer goods such as laundry baskets, storage containers, and sink stoppers.³⁹ In industrial applications, such as scents for hotels, offices and public areas, fragrances are encapsulated in both polymers and fibers.³⁹ Controlled fragrance diffusion systems are used in amusement park attractions for an 'extra-sensory' experience.³⁹

Fragrances are also being used to mask unpleasant odors in applications such as garbage bags or household chemical containers.³⁹ In trash bags, citronella fragrance both masks odor and keeps insects away.³⁹ Fragrances such as cedar can be used after renovating computer rooms or offices to mask the odor remaining from materials in wire and cable and other new plastics.³⁹ In PVC, fragrances are used to cover the smell of sulfur based stabilizers.³⁹

Suppliers are seeing an increased interest in deodorants that can be used to absorb volatile organic compounds such as malodors or unwanted vapors from plastic articles, rather than simply masking them with a pleasant scent.³⁹ Deodorants consist of dispersions of microporous inorganic materials in a polymer carrier.³⁹ Inorganic materials with specific ranges of pore sizes are selected, depending on the type of vapor to be absorbed.³⁹

The multimedia media output devices, controlled by a computer, may comprise, for example, a display device, a speaker, a mobile wireless communication device, an odor output device, a tactile output device, a body stimulating electrode, a moving and/or vibrating chair, a heating and/or cooling system, a fan, a flavor dispenser, a liquid sprayer, and/or any other device capable of providing outputs that stimulate one or more user senses.⁴⁰

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(but without actually removing any of the PDMS material), which elastically keeps the hole tightly closed if unactivated, but opens allowing the gas/odor release when activated by electrical heater lines.³⁷

A novel controlled release system for the delivery of essential oil used as ambient odors was proposed.³⁸ The interactions of cyclodextrins and β -cyclodextrin polymers with linalool and camphor in *Lavandula angustifolia* essential oil were investigated.³⁸ Cyclodextrin polymers reduce the volatility of the aroma compounds and stable

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DISTINCTIVE ODORS

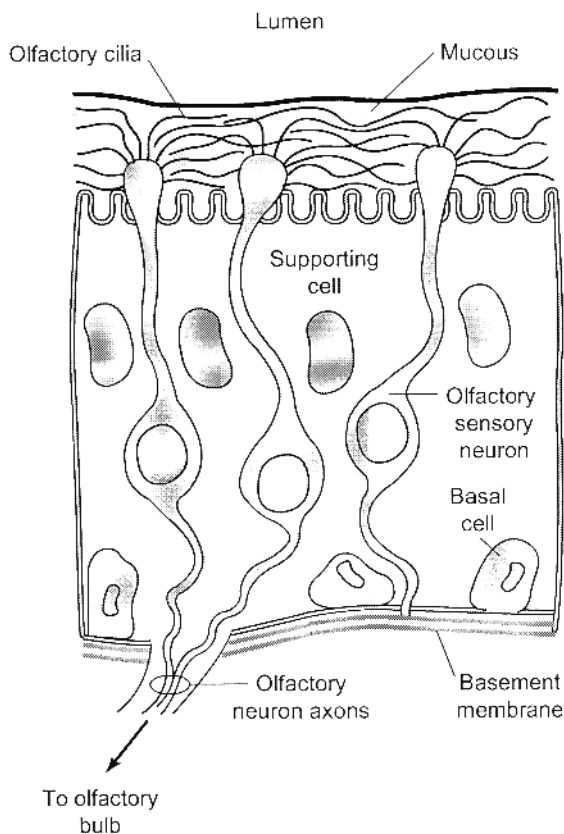


Figure 3.1. A schematic diagram of the olfactory epithelium. Odorants enter the nasal cavity, diffuse through the nasal mucous and interact with specific receptors on the dendritic cilia of olfactory sensory neurons. The signals initiated by this receptor binding are transduced into electrical signals within the cilia and are transmitted along the sensory neuron axons to the olfactory bulb in the brain. [Adapted, by permission, from Munger S D in *Molecular Basis of Olfaction and Taste*, **Basic Neurochemistry**, 8th Ed., Elsevier, 2012.]

Humans can smell many thousands of odorants with high precision (even slight changes in odorant structure are noticed by our sense of smell). Figure 3.1 shows the mechanics of action of the olfactory system. The olfactory epithelium contains three predominant cell types: the olfactory sensory neurons; the supporting cell; and the basal cell.¹ Cilia contain the molecular machinery of olfactory transduction, including receptors, effector enzymes and ion channels.¹ Cilia capture odorant characteristics and transmit them further through olfactory neuron axons to the olfactory bulb.¹ Olfactory bulb cells help to shape sensory input and olfactory bulb output in several ways before this information is sent to higher centers in the brain.¹ Humans are known to have 350 odorant receptors, which are able to recognize chemically diverse odorants.¹ Odor discrimination involves a very large number of different odorant receptors, each responsive to a small set of odorants.¹ Odorant receptors can have a broad receptive range.¹ They can respond to more than one odorant, and often to odorants of more than one chemical class (e.g., aldehydes and alcohols).¹ More than one odor receptor can be activated by the same odorant.¹

Also, not every odorant receptor, activated by a particular odor, responds with the same efficacy to that odor.¹ The identity of an individual odor is encoded by several differently tuned odorant receptors and it is called a combinatorial odor code.¹ The olfactory system responds to extremely low concentrations of odorants, and olfactory perception is believed to be extremely sensitive.¹ It is theoretically possible that the limit of olfactory detection is a single molecule.¹ More details on the mechanisms of operation of our sense of smell can be found elsewhere.¹

In the separate sections below, different distinctive types of odors will be analyzed from the point of view of their origin (material or product in which this odor is formed) and the chemical composition of odorants which cause the formation of this distinctive odor in different materials.

3.1 SWEET, BLOSSOM-LIKE (FRUITY)

Sweet odor and taste is the most popular distinctive odor type detected. It is also frequently called blossom-like or fruity. Table 3.1 contains information on sources of odor, products in which odor was detected, and chemical composition of odorants most likely causing this odor.

Table 3.1. Sources of sweet odor.

Source	Product	Odorants	Refs.
Epoxy liner	Drinking water	phenol, styrene, benzaldehyde	6
HDPE	Water	ethyl propane	12
HDPE pipe	Water	phenol	11
Oil sands	Water	naphthenic acids	10
Polypropylene		unknown, d-undecalactone (peach-like), d-dodecalactone (peach-like)	5
PVC pipe	Drinking water	cycloheptane, 2-methyl cyclopentanone, 2-octanoic acid methyl ester, 4-nitrobenzofuran, 4-(1,1-dimethyl) cyclohexanol, 2-heptadecanone, 3-hydroxybenzaldehyde	7
Refillable PET bottles	Water & soft drinks	2-methoxynaphthalene	3
Silane cross-linked PEX pipe	Drinking water	2-ethoxy-2-methylpropane (23 to >100 µm/g)	2
Triolein & trilinolein		2-propylfuran, 4-nonyne, heptanal, 2-pentylfuran, octanal, nonanal	4
Water reservoir	Water	chlorine	8
	Indoor	acrylic acid	13
	Wine	2-phenylethyl acetate, linalool	9
Pineapple		methyl 2-methyl butanoate and ethyl 2-methyl butanoate	20
Gewürztraminer	Wine	standard and late harvest (but not icewine)	21

Table 3.1. Sources of sweet odor.

Source	Product	Odorants	Refs.
Strawberry	Vinegar	sweet and fruity characteristics in vinegars from wood barrels	22

3.2 GRASSY

Table 3.2 contains information on sources of odor, products in which this odor was detected, and chemical composition of odorants most likely causing this odor.

Table 3.2. Sources of grassy odor.

Source	Product	Odorants	Refs.
Ham		dimethyltrisulfide, nonanal, 2-nonenal	14
Polypropylene		hexanal, (Z)-hex-3enal	5
Triolein and trilinolein		pentanal, hexanal, 3-hexanol, (E)-2-hexenal, (E)-4-nonenal	4
Strawberry	Vinegar	grassy characteristics were predominant in vinegar from glass containers	22

3.3 LIQUORICE

Liquorice (licorice) is a Mediterranean herb which has roots having an astringent flavor that is extracted to mask unpleasant flavors, such as drugs.

A refillable poly(ethylene terephthalate) bottle was a source of off-odor in mineral water and soft drinks.³ Anetole was the substance detected, which was associated with liquorice odor.³

Trans-4-methylcyclohexylmethanol has a 2000-fold lower odor threshold concentration than *cis*-4-methylcyclohexylmethanol with odor descriptors of licorice and fermented-fruit, respectively.²³

Table 3.3 contains information on sources of odor, products in which this odor was detected, and chemical composition of odorants most likely causing this odor.

Table 3.3. Source of liquorice odor.

Source	Product	Odorants	Refs.
Crude	spill	4-methylcyclohexylmethanol	23
Licorice roots		e-nose licorice odorprint developed for roots from different locations (China, Iran, Italy, Turkey	24

3.4 PETROLEUM/PHENOLIC

Table 3.4 contains information on sources of odor, products in which this odor was detected, and chemical composition of odorants most likely causing this odor.

Integrated bioremediation process for the removal of petroleum hydrocarbons and the mitigation of odor induced by reduced sulfur from contaminated marine sediment was developed.²⁵ A method was developed for identification of source of spills of petroleum products based on the composition of the polycyclic aromatic sulfur heterocycles.²⁶

The odor characteristics and odor threshold concentrations of ortho- and para-halogenated phenols, and the corresponding di-halogenated phenols, were investigated. The ortho-halogenated compounds tend to elicit a medicinal odor and the smell of para-halogenated compounds was mostly fecal and horse stable-like, comparable to that of 4-methylphenol.²⁷

Table 3.4. Sources of petroleum odor.

Source	Product	Odorants	Refs.
PVC pipe	Drinking water	cycloheptane, 2-methylcyclopentanone, 2-(2,4-dichlorophenoxy)-N,N-dimethyl acetamide, oxime cyclopentanone	7
Refillable PET bottles	water and soft drinks	benzene, toluene, xylene, naphthalenes (expected source – customer misuse)	3
Silane crosslinked PEX pipe	Drinking water		2
Vinyl-based coating	Water in food plant	styrene, acetone, 2-ethoxy-2-methylpropane, and methyl isobutyl ketone	15

3.5 “PLASTIC”

Table 3.5 contains information on sources of odor, products in which this odor was detected, and chemical composition of odorants most likely causing this odor.

Sensory tests showed performance differences among four freezer plastic bags.²⁸ There were substantial differences of aroma transfer properties among the plastic bags.²⁸

Odor testing was used as a tool to detect early degradation of polymeric materials.³⁰ Polyamide 66 was selected as a model material, because it is frequently used at elevated temperatures, and subjected to accelerated ageing through thermooxidation.³⁰ The odor intensity correlated with a deterioration in mechanical properties.³⁰ Eight degradation products were determined.³⁰ The relationship between the odor and the degradation of mechanical performance was detected at a very early stage of degradation before any significant changes could be observed in thermal and surface properties.³⁰

Table 3.5. Sources of “plastic” odor.

Source	Product	Odorants	Refs.
Epoxy liner	Drinking water	total organic carbon	6
Ham		vinyl acetate, toluene, nonanal	14

Table 3.5. Sources of “plastic” odor.

Source	Product	Odorants	Refs.
LDPE	Food	1,3-di-tert-butylbenzene or 2,4-di-tert-butylphenol	17
Oil sands	Water	naphthenic acid	10
Polyethylene	Food & beverage	8-nonenal	16
Poly(ethylene terephthalate)	Food	1,3-di-tert-butylbenzene or 2,4-di-tert-butylphenol	17
Polypropylene		(Z)-dec-2-enal	5
Silane crosslinked PEX pipe	Drinking water	2-ethoxy-2-methylpropane	2,29
Triolein trilinolein		1,4-pentadien-3-ol, (E or Z)-2-octene, (Z)-2-nonenal, (E)-2-nonenal, 2-decanone, 2-decyn-1-ol, (E)-2-decenal	4
	Indoor environment	styrene (building materials)	13
	Wine	unknown	9
Mulch film		soil pollution by plastic mulches: microplastics, phthalates, agrochemicals	31

3.6 MEDICINAL

Table 3.6 contains information on sources of odor, products in which this odor was detected, and chemical composition of odorants most likely causing this odor.

Table 3.6. Sources of medicinal odor.

Source	Product	Odorants	Refs.
Oil sands	Water	naphthenic acid	10
PVC pipe	Water	S-sec-butyl ester-1-thio-acetoacetic acid	7
	Indoor environment	iodine solution	13
o-halogenated compounds			27
Water		2-bromophenol, 2,4-and 2,6-dibromophenol gave medicinal taste to water from desalination plant	32
Adhesives	Food packaging	1-butanol	33

3.7 CHEMICAL

Table 3.7 contains information on sources of odor, products in which this odor was detected, and chemical composition of odorants most likely causing this odor.

Table 3.7. Sources of chemical odor.

Source	Products	Odorants	Refs.
HDPE	Water	cyclohexanone, cycloheptanone	6
HDPE granulate		C ₇ -ketone	12
	Indoor environment	bleach	13
Wastewaters		benzothiazole, ethanol	34

3.8 ETHANOL WITH FUSEL OIL

Fusel oil is an acrid oily liquid with an unpleasant odor. This distinctive odor was associated with 3-methyl-1-butanol, isobutyl alcohol, isopropyl, and propyl alcohol.³ This distinctive odor was found in reused PET bottle, which was likely used for storing alcohol distillate.³

3.9 FATTY/WAXY

Table 3.8 contains information on sources of odor, products in which this odor was detected, and chemical composition of odorants most likely causing this odor.

Taste quality responses for linoleic acid were fatty/oily/waxy, or bitter.³⁷ Humans can detect long-chain fatty acids by both olfactory and non-olfactory pathways when these hydrophobic molecules are delivered to the oral cavity.³⁷

Table 3.8. Sources of fatty (waxy, putty) odor.

Source	Products	Odorants	Refs.
LDPE		1,3-di-tert-butylbenzene, 2,4-di-tert-butylphenol	17
Polypropylene		(Z)-non-2-enal, (Z)-non-4-enal	5
Triolein trilinolein		2-heptanol	4
Sewer manholes		butyric, isovaleric, valeric acids	35
Cosmetic creams		sensory attributes: sticky, difficult to spread, easy to spread, white residue, fresh, smooth, waxy, greasy, and oily	36

3.10 MOLDY/MUSTY

Table 3.9 contains information on sources of odor, products in which this odor was detected, and chemical composition of odorants most likely causing this odor.

Musty odor is one of the most usual taints in water and wine linked to microorganism activity.³⁸ The volatile compounds responsible for a moldy off-aroma include approximately 20 compounds, namely, haloanisoles, geosmin, 2-methylisoborneol, several alkyl-methoxypyrazines, 1-octen-3-ol, 1-octen-3-one, *trans*-octenol, 3-octanone, fenchol and fenchone.³⁸ These compounds are present at very low levels and have very low sensory thresholds.³⁸ Their analysis requires preconcentration and highly sensitive GC detectors.³⁸

The US Environmental Relative Moldiness Index scale was tested in France in twenty homes in Brittany.³⁹ The results suggest that the same 36 fungi may be useful in creating index in France.³⁹

Table 3.9. Sources of moldy (musty) odor.

Source	Product	Odorants	Refs.
Epoxy liner	Water	total organic carbon	6
Ham		2-ethylphenol	14
Reused PET bottle	Water	geosmin, trichloroanisoles, chlorophenols, alkoxy-pyrazines	3
Polypropylene		hexanoic acid	5
Triolein trilinolein		3-hexanone	4
	Indoor environment	benzoquinone	13
	Water	2-isopropyl-3-methoxypyrazine, geosmin	8
	Water	geosmin	19
Cork	Wine	2,4,6-tribromoanisole	18
Coffee		1-octen-3-ol	40

3.11 SEWER/ROTTEN

Table 3.10 contains information on sources of odor, products in which this odor was detected, and chemical composition of odorants most likely causing this odor.

The photocatalytic degradation of 2-isopropyl-3 methoxy pyrazine, a common metabolite of soil *Actinomyces* which contributes a rotten vegetable odor to water, was investigated under simulated solar irradiation.⁴² Almost complete detoxification of the irradiated solution can be achieved.⁴²

Botrytis cinerea infection contributes to improvement of wine quality by the so-called “noble rot”.⁴³ Molecules such as 1-octen-3-ol, phenylacetaldehyde and furaneol were positively linked to the noble-rotten grapes.⁴³

Table 3.10. Sources of sewer (rotten, fecal) odor.

Source	Product	Odorant	Refs.
Refillable PET bottles	Water	dimethyl disulfide	3
	Indoor environment	indole	13
Bottled water		organic sulfur and selenium compounds	41

3.12 ANIMAL

Table 3.11 contains information on sources of odor, products in which this odor was detected, and chemical composition of odorants most likely causing this odor.

Table 3.11. Sources of animal odor.

Source	Product	Odorant	Refs.
Ham		2-ethylphenol, heptanoic acid, octanoic acid	14
Polypropylene		4-methylphenol	5

3.13 CHEESY/BUTTERY

Table 3.12 contains information on sources of odor, products in which this odor was detected, and chemical composition of odorants most likely causing this odor.

Table 3.12. Sources of cheesy (buttery) odor.

Source	Product	Odorant	Refs.
Ham		3-methyl-1-butanol, 3-methyl-butanoic acid	14
Polypropylene		butanoic acid, 2-methylpropanoic acid, pentanoic acid, 2-methylpentanoic acid, 4-methylpentanoic acid	5
Triolein trilinolein		1-methyl-2-(4-methylpentyl)-cyclopentene	4
Buttery odor compound		acetoin (3-hydroxy-2-butanone)	44

3.14 SMOKY, BURNT

Table 3.13 contains information on sources of odor, products in which this odor was detected, and chemical composition of odorants most likely causing this odor.

Under good combustion conditions, the burnt smell patterns resulting from a single material were very consistent, mostly dominated by methylphenols or naphthalene.⁴⁵

Table 3.13. Sources of smoky (burnt) odor.

Source	Product	Odorant	Refs.
Polypropylene		hexanoic acid	5
Silane-cross-linked PEX pipe	Drinking water	2-ethoxy-2-methylpropane	2
	Wine	4-ethyl guaiacol, 4-vinyl-2-methoxy-phenol, 2,6-dimethoxyphenol	9

3.15 METALLIC

γ -Irradiation of polypropylene produced a metallic odor.⁵ Metallic odor is associated with the following volatile compound: 4,5-epoxy-(E)-dec-2-enal.⁵

The sensory experiments indicated that (E)-4,5-epoxy-(E)-2-decenal, (E,E)-2,4-octadienal, and 1-octen-3-one are the main contributors to the metallic, cucumber, and mushroom notes of the rainbow trout.⁴⁶

3.16 SOUR OR ACRID

Table 3.14 contains information on sources of odor, products in which this odor was detected, and chemical composition of odorants most likely causing this odor.

Table 3.14. Sources of sour or acrid odor.

Source	Product	Odorant	Refs.
Polypropylene		acetic acid, butanoic acid, 2- and 3-methylbutanoic acid, hexanoic acid.	5
Triolein trilinolein		(Z)-2-decenal	4

3.17 MINTY

Minty odor was detected in volatile products of thermal degradation of triolein, which was selected to study odors produced by higher oleic acid-containing oils.⁴ Minty odor produced by thermal degradation of triolein was associated with emission of tetrahydro-2-methyl-2-furanol and 5-propyl-dihydro-2-(3H)-furanone.⁴ Menthol is a cyclic monoterpene alcohol which possesses cooling characteristics and a minty smell of the oil remnants from which it was obtained.⁴⁷ Natural menthol is isolated exclusively from *Mentha canadensis*, but can also be synthesized on industrial scale through various processes.⁴⁷

3.18 COCONUT

Table 3.15 contains information on sources of odor, products in which this odor was detected, and chemical composition of odorants most likely causing this odor.

Ethanol increases finish intensity and duration of coconut and floral flavors in red wines.⁴⁸ Floral and coconut notes interact, diminishing the intensity and duration of coconut finish.⁴⁸

Table 3.15. Source of coconut odor.

Source	Product	Odorant	Refs.
Polypropylene	γ-irradiation	γ-nonalactone	5
Triolein	thermal degradation	(E)-2-undecenal	4

3.19 CARDBOARD-LIKE

Cardboard-like odor was identified in volatile products of γ-irradiation of polypropylene.⁵ The following volatile compound was associated with a cardboard-like odor: (E)-non-2-enal.⁵

3.20 MUSHROOM-LIKE

Mushroom-like odor was identified in volatile products of polypropylene.⁵ The following volatile compounds were associated with mushroom-like odor: oct-1-en-3-one, non-1-en-3-one.⁵ γ-Irradiation causes decrease of concentration of both products.

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TASTE

The recognition of food flavors is a result of a combination of taste, olfactory (odor), and somatosensory. The somatosensory system is composed of the receptors and processing centers which produce sensory modalities such as touch, temperature, proprioception (body position), and nociception (pain). Touch also includes “mouth feel”, which is provided by the texture of food. The thermoreception and nociception is caused by pungent spices and irritants.¹

It is pertinent from the above that recognition of food flavors requires a magnitude of reception cells, which utilize different molecular mechanisms to detect and distinguish the different components of flavor. Figure 4.1 shows the structure of the tongue, taste papillae, and taste buds, which participate in recognition of taste.

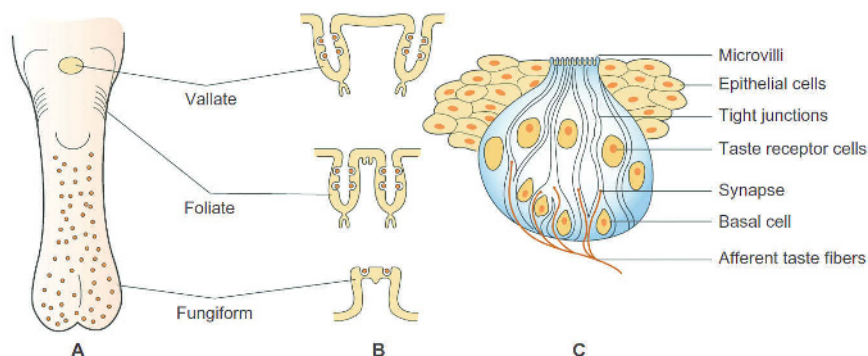


Figure 4.1. Tongue, taste papillae and taste buds. (A) Surface of the rat tongue showing the location of the taste papillae. (B) Cross-section of the three main types of taste papillae: fungiform, foliate and (circum) vallate. (C) Taste buds contain taste receptor cells, TRCs, and basal cells. Taste receptor proteins present on the microvilli of TRCs respond to tastants in the oral cavity, initiating a transduction cascade that results in the release of neurotransmitter onto afferent cranial nerve fibers, which carry taste information back to the brainstem. [Adapted, by permission, from Munger S D in *Molecular Basis of Olfaction and Taste*, **Basic Neurochemistry**, 8th Ed., Brady S T, Siegel G J, Albers R W, Price D L, Eds., *Elsevier*, 2012.]

The chemical detection of taste stimuli resides in specialized epithelial cells, taste receptor cells.¹ Taste buds contain clusters of 50 to 100 taste receptor cells (Figure 4.1c).¹ They reside within connective tissue specializations called fungiform, foliate and circumvallate papillae of the tongue (Figure 4.1.a).¹ Taste receptor cells are also found in the palate, pharynx, and upper portion of the esophagus.¹ Solutes in the oral cavity make contact with the apical membranes of the taste receptor cells *via* the taste pores.¹

Taste perception recognizes the following distinctive components of flavor: sweet, sour, salty, bitter, and umami (the taste of glutamate).¹

Sense of taste can detect and discriminate among various ionic stimuli, for example, Na^+ as salty, H^+ as sour, sugars as sweet and alkaloids as bitter.¹ Figure 4.2 shows a model for the major signaling mechanism for transduction of different taste stimuli.¹

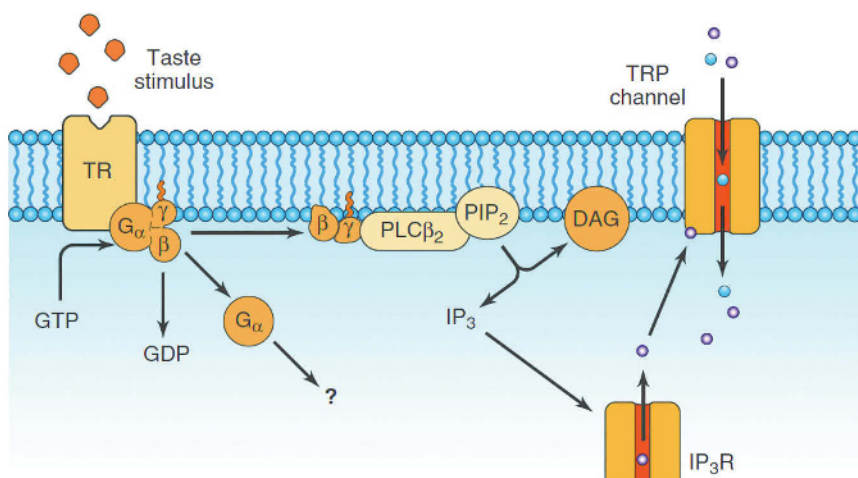


Figure 4.2. A model for the major signaling mechanisms for the transduction of sweet, bitter and umami stimuli. Note that stimuli of each of these taste qualities interact with G protein coupled receptors: bitter stimuli with taste receptors T2Rs, and sweet and umami stimuli with taste receptors T1Rs. α -Gustducin has been implicated in the transduction of all three types of stimuli, but other α -subunits likely also couple to T1Rs or T2Rs in some taste receptor cells populations. PLC- β 2 and the Ca^{2+} -activated taste receptor cell channel subunit TRPM5 are essential for normal sweet, bitter and umami taste. The role of IP3 and the IP3R in the stimulus-dependent increase in intracellular Ca^{2+} . [Adapted, by permission, from Munger S D in *Molecular Basis of Olfaction and Taste*, **Basic Neurochemistry**, 8th Ed., Brady S T, Siegel G J, Albers R W, Price D L, Eds., Elsevier, 2012.]

The first taste-specific G protein-coupled receptors were identified in 1999 but remained the only known receptors for several years.¹ Now they are called T1R1 and T1R2.¹ These receptors are Class C G protein-coupled receptors.¹ T1R1 (sweet and umami taste receptor) is found predominantly on the anterior tongue and T1R2 (bitter taste receptor) mostly on the posterior tongue.¹

Sour taste is a function of the acidity of a solution, depending primarily on the proton concentration and to a lesser extent on the particular anion involved.¹

It was stated in the beginning that flavor perception is a combination of different systems and receptors. The systems are not completely independent as they can increase or decrease the signal of individual systems. Cross-modal sensory integration is frequently inferred from the influence of one modality on responses to another.² Commonly, this is an enhanced (sometimes supra-additive) response to information from one sensory system due to concurrent input from another modality.²

The most obvious example of odor–taste interactions is attributed to odors of qualities that are associated with basic tastes.² For example, the odor of caramel or vanilla is most frequently expressed by the term “sweet-smelling”; similarly, “sour” is used for the odor of vinegar.² The possession of taste properties by odors is almost universal, particularly in the case of commonly consumed foods.² For some odors, taste qualities may represent the most consistent description used, and ratings of taste descriptors for odors.²

Reciprocal effects of odors on tastes are known.² For example, sweet taste is enhanced in the presence of an orthonasally-presented congruent odorant (strawberry).² Similar enhancements were found in the case of raspberry and water chestnut.² Apple flavor is a collection of different inputs, such as tastes (sweet, sour), textures (crisp, juicy), and odor (lemony, acetone-like, honey).² A more precise way of conceptualizing flavor, therefore, is that cross-modal sensory signals are combined to produce a percept.²

All the above studies are still in relative infancy and only general concepts and mechanism are understood.

Many plastic materials are processed by thermal treatment, which changes their composition. In many cases this change of composition causes a change of the taste of products which come into contact with thermally processed packaging materials. Many aldehydes (formaldehyde, acetaldehyde, propanal, propenal, butanal, and other higher aldehydes) are found in smoke from extruded polyethylene.³ Also, various ketones (propanone, 2-butanone, 2,4-pentadione, 2-pentanone, 3-methyl-3-pentene-2-one, 3-pentanone, 2-methyl-3-hexanone, 2-methylcyclohexanone, 3-hexanone, 3-methylcyclohexanone, 4-methylcyclohexanone, 2-heptanone, 4-heptanone, 3-heptanone, 3-methyl-3 heptanone, 4-heptanone, 2-octanone, 3-octanone, 2-nonanone, 5-nonanone, 3-decanone, 3-undecanone, and 3-dodecanone) are found in the smoke at the die orifice for extruded films of polyethylene.³ Some carboxylic acids (acetic acid, propionic acid, butanoic acid, pentanoic acid, hexanoic acid, heptanoic acid, octanoic acid, nonanoic acid, decanoic acid, undecanoic acid, and dodecanoic acid) are also identified in smoke coming from die orifice for extruded films of polyethylene.³ The amounts of these products depend on extrusion temperature and film thickness.³ Volatile products are partially retained in films and they contribute to bad odor and taste in packaging material applications.³

Descriptive attributes of odor and taste frequently differ. Here is an example of odor and taste evaluation in HDPE: odor attributes selected by the test panel were sweet, chemical, stale, dusty, foul and floor-cloth, and the attributes for taste were: sweet, metallic, stony, pungent, dusty, plastic, foul, stink bug, and candle grease.⁴

Changes of taste may also come from water due to the action of microorganisms, as, for example, 2-methylisoborneol and geosmin are products from algae decomposition and, depending on their concentration, can be toxic; otherwise, they give unpleasant taste and odor to water.⁵ For water treatment companies it is important to constantly monitor their presence in the distributed water to avoid customer complaints.⁵

Taste changes come from additives. For example, the presence of thioesters in polypropylene changes taste of products in contact with such polypropylene.⁶ It is common to crosslink polypropylene using various peroxides. It was found that use of di-tertiary-amyperoxide improves taste of products in contact with reacted polypropylene as compared with polypropylene in which 2,5-dimethyl-2,5-di-t-butylperoxyhexane was used for crosslinking.⁶

Taste producing substances can be eliminated. Taste change in plastic material can originate from polymerization or thermal and radiation treatment. The addition of zeolites (among many other absorbents) were found to be useful in elimination of taste in plastic film/sheeting used in packaging of foodstuffs and pharmaceutical preparations.⁷

Taste and olfaction are susceptible to adaptation (i.e. the progressive reduction in the appreciation of a stimulus during the course of continual exposure to that stimulus).⁸ Perception of a substance goes away in seconds.⁸ The cells of the taste buds undergo renewal, having a life span of about 10 days (the taste bud is made up of 50 to 150 cells arranged to form a pear-shaped organ; the lifespan of these cells is 10 to 14 days; they are constantly being renewed from dividing epithelial cells surrounding the bud¹¹).⁸ The renewal is modulated by nutrition, hormones, and age, and other factors such as drugs and radiation.⁸ The following factors influence the perception of taste and differences between perceptions of humans:⁸

- genetics (sensitivity to the bitter taste of phenylthiourea is genetically determined; some people are genetically unable to smell fish; other people, having the increased number of taste papillae have extreme sensitivity to n-propylthiouracil, which causes that they do not to like green vegetables and fatty foods)^{8,10}
- hormones (the sense of taste may vary because of the menstrual cycle or may be distorted during pregnancy; well-known cravings for unusual foods)⁸
- age (the number of taste buds declines with age; the function of ion channels and receptors also alters with age; foods disliked when young become acceptable or even favorite later in life)⁸
- drugs (taste can be suppressed by the local anaesthetic; gymnemic acid (from the Indian tree *Gymnema sylvestre*) decreases sweet perception; the active compounds of artichokes, chlorogenic acid and cynarin, suppress sour and bitter taste receptors and enhance performance of sweet taste receptors; or miracle fruit *via* an active ingredient, miraculin, changes perception of the sour taste to the sweet taste).⁸
- shortage of a certain substance may lead to a perceived increase in palatability of this substance (it increases driving forces to compensate for this nutritional imbalance; sweet and salty taste sensitivities in peripheral taste organs are affected by endogenous humoral factors, e.g., leptin and endocannabinoids, mediators of hypothalamic circuits underlying motivational aspects of feeding behavior, inhibit and enhance sweet taste sensitivity, respectively)⁹
- humoral factors (the obese diabetic mouse lacking functional leptin receptors shows enhanced neural responses and behavioral preference to sweeteners;⁹ fat taste sensitivity is impaired in obese individuals¹²)
- taste disorders (taste and smell disorders are observed after heart, neurological, respiratory and liver problems)¹³

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FOGGING

Fogging is a phenomenon commonly observed in applications of plastic materials in automotive applications, food packaging and agricultural sectors, and on indoor appliances. The name of this phenomenon comes from fog formed as a result of water vapor condensation, forming small droplets on the surface of plastic materials or glass when air cools to the temperature below the dew point of the fogging-causing substances.

In the automotive industry, condensation of volatiles from the interior parts of cars on the car windows results in a sticky and greasy film, which impairs the driver's sight.¹ This highly undesirable phenomenon can only be averted by avoiding emitting materials in the car interior.¹ In addition, some monomers or low-molecular-weight compounds from polymer may be harmful or may smell.¹

In agriculture and food packaging, fogging obstructs light transmission and diminishes the amount of light transmitted through the agricultural film or the ability to see contents of food packages.² In agricultural film, fogging caused a condensation problem, and in food packaging it is especially visible on food packages stored in chilling cabinets.² The severity of fogging also depends on temperature and relative humidity of the air mass and temperature of plastic film.² In addition, the undesirable effects not only include reduced total light transmission in greenhouses, but also water dripping that can lead to plant damage.² Plant damage may be induced by the focussing effect of the water droplets as an array of lenses concentrating solar energy on foliage.² The end result of all these effects for food producers is a lower potential yield and reduced product quality.²

Fogging in an indoor environment has two negative influences. Similar to the above cases, it obstructs the light transmission due to the condensation of vapor of condensing substances on the surface, but it also forms high concentration areas on the surface of the many indoor appliance of condensing substances, which, when they evaporate, are harmful for inhabitants.³

The above examples show that fogging is important for the subject of this book because concentrating volatile substances on the surfaces used for their condensation may contribute to retention of odor-causing substances which may be retained in the environment (car interior, indoor conditions, or hot-house interior) and contribute to the permanent odor in these environments.

Deposition of a liquid substance on the surface of glass or plastic film causes changes in refractive index because light has to travel through two layers of material and it gets partially reflected and refracted according to the proportion of refractive indices of both layers. Also, deposition of liquid droplets of condensed substances changes surface tension of glass or plastic film.² In the case of plastic film, it is less severe because plastic films without anti-fogging additives are highly hydrophobic and they have low surface

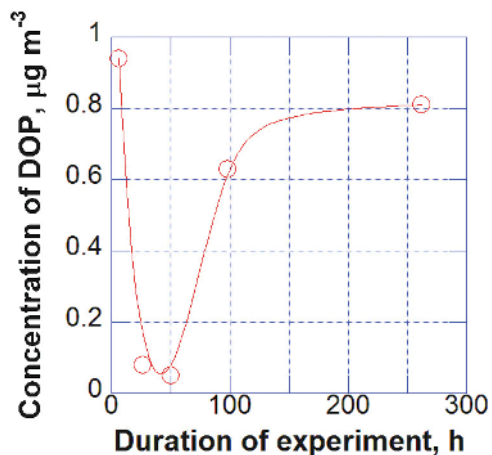


Figure 5.1. Concentration of DOP in air of the testing chamber in fogging experiment vs. duration of experiment. [Data from Wensing M, Uhde E, Salthammer T, *Sci. Total Environ.*, **339**, 19-40, 2005.]

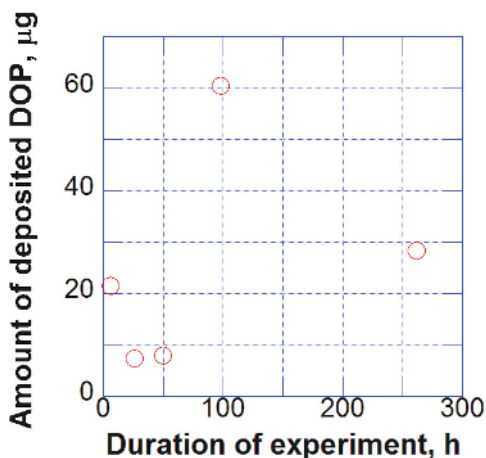


Figure 5.2. Amount of deposited DOP on 450 cm^2 of condensation surface area vs. duration of fogging experiment. [Data from Wensing M, Uhde E, Salthammer T, *Sci. Total Environ.*, **339**, 19-40, 2005.]

energy (30 MJ/m^2) as compared with water (72 MJ/m^2).² Because of this difference, water condenses into small droplets, having a high contact angle.² Similar is the case of condensation on the surface of condensed volatile components which also have low surface energy.

In the fogging test, semivolatile organic compounds such as plasticizers and flame retardants are precipitated inside the chamber on a cooled surface.³ This method has been developed for examining automotive parts to determine fogging-active substances.³ It is also used for examining products used indoors and it permits estimation of the emission of semivolatile organic compounds condensed on surfaces.³ The difference is in the test temperature used. In the automotive sector, a test chamber method developed for examining individual car components (instrument panel, seats, etc.) is used at test temperatures of 65 and 100°C.³ In indoor applications, the same test method is used at room temperature (23°C).³ It is observed during studies that the boiling point of a substance makes a difference in its behavior. Compounds having boiling points between 290 and 400°C tend to condensate on surfaces and therefore can be detected only at very low concentrations in the gas phase (in surrounding air).³ Because of high boiling points, most of the phosphoro-organic compounds (flame retardants) and phthalates (plasticizers) belong to the semivolatile organic compounds.³ These substances are essentially adsorbed on solids surface, either indoor equipment or dust particles.³ Figures 5.1 and 5.2 show concentrations of di(2-ethylhexyl) phthalate in air and condensed on surface of test equipment, respectively.³

Emission of volatiles is governed by partitioning between the gas and the sample phase rather than by full evaporation of the volatile compound.¹ In testing of different grades of polypropylene, alkanes, alkenes, and dialkenes were the reason for fogging.¹ Emissions from polypropylene may cause the undesired smell, be harmful, or lead to fogging, which prohibits its use for car interiors.¹

Additives used in processing TPO resins may cause fogging. Special additive was developed for soft touch, high impact TPO resin used in the production of automotive steering wheels.⁴

A new foam is suitable for a number of automotive gasketing applications.⁵ It satisfies the SAE J-1756 specification for fogging test.⁵

Non-fogging fragrances for vehicles have been patented.⁶ Fragrance is composed of solvent, aroma, and surfactants.⁶ Aroma substances which pass the fogging test include: D-limonene, tangerine oil, and lilyal.⁶

A low fogging component of skin formed on plastic materials contains polymer or copolymer of butyl acrylate.⁷ This is a replacement component for NBR rubber usually added to PVC as an internal plasticizer.⁷

Anti-fogging additives used in food packaging and agricultural films differ.² In agricultural film, water is constantly running along the surface of the film and it may wash out additive, therefore water-insoluble additive should be selected.² In addition to solubility, additive should be thermally stable and compatible with polymer used for film production.² In these applications, mostly nonionic surfactants are employed as anti-fogging additives.²

Low-emission polyurethane soft foams are required in many applications. They provide low odor and reduced fogging.⁸ One such solution was developed from a combination of polyisocyanates and polyols have at least two hydrogens which are reactive toward the isocyanate group.⁸ Also, special treatment of polyether polyols after they were synthesized leads to low-fogging polyurethane foams.⁹ This treatment involves thermal distillative step in countercurrent column.⁹

Anti-fogging thermoplastic resin sheet can be obtained by coating containing cyclodextrin or water soluble compound in which hydroxyl groups of cyclodextrin are modified.¹⁰ In another invention, the anti-fogging article is developed from crosslinked resin having saturated water absorption of at least 45 mg cm^{-3} and contact angle of at least 30° .¹¹ Photocurable composition for forming an anti-fogging coating comprises urethane compound having at least two (meth)acryloyl groups and a polyoxyalkylene chain, compound having at least two (meth)acryloyl groups and at least two hydroxyl groups, a compound having an ethylenic unsaturated group other than previous two compounds, and initiator.¹²

Anti-fogging film was obtained from isosorbide-based epoxy polymer.¹³ The film was applied by spin coating and subsequent thermal polymerization on the surface of the glass.¹³ The anti-fogging performance is attributed to the strong hydrogen bonding between the hydroxyl groups in the polymer and the water molecules.¹³

The quaternized cellulose and carboxymethyl cellulose were layer-by-layer assembled to prepare a thin film.¹⁴ The film exhibits anti-fogging and anti-frosting behaviors because of moisture adsorption into the film matrix.¹⁴

Baerlocher GmbH has introduced a new generation of kickers that emit reduced levels of volatile organic compounds.¹⁵ The low-VOC Baerostab KK-432 is suitable for the automotive supply industry, flooring and wallpaper.¹⁵ Also, Lanxess has launched two halogen-free flame retardants for use in flexible polymer foams.¹⁶ The new grades are based on phosphorus chemistry.¹⁶ They are characterized by low fogging and scorching, making them useful in the furniture and automotive industries.¹⁶ Momentive Performance Materials introduced Niox flame lamination additive, FLE-500.¹⁸ The product meets strict

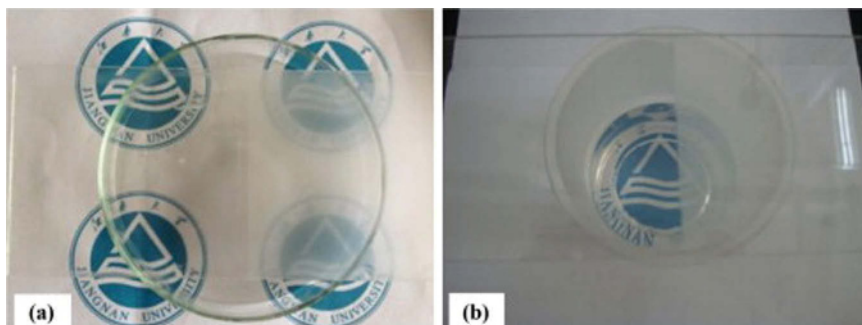


Figure 5.3. Anti-fog tests of acrylate formulation containing sulfonic acid groups on polycarbonate plate. (a) Anti-warm fog test and (b) anti-cold fog test. The left part of the plate is coated with the anti-fog coating and the right one is without. [Adapted, by permission, from Yuan, Y; Liu, R, Wang, C; Luo, J; Liu, X, *Prog. Org. Coat.*, 77, 4, 785-9, 2014.]

fogging and emission specifications for flame and heat lamination of polyether foams by improving the total emission levels of the finished foam goods.¹⁸ Tosaf has expanded its family of anti-fog masterbatches for the packaging industry.²⁰ Designed for packaging films and sheets, the two new grades are food contact approved, adjusted for optimal processing, and extended anti-fog activity in polyolefins.²⁰ Tosaf also manufactures anti-fog/anti-drip masterbatch AF0406PE for greenhouse films.²¹ The product has been especially developed for hot climates.²¹

The hydrophilicity of flame-made SiO_2 nanowires and the special fibrous structure, the nanofibrous SiO_2 film exhibits considerable anti-fogging and anti-reflective properties.¹⁷ Flame made nanofibrous films show tunable wetting and optical performance.¹⁷

UV curable hydrophilic acrylate polymers containing sulfonic acid group were prepared *via* free radical copolymerization using 2-acrylamido-2-methyl propane sulfonic acid as hydrophilic monomer and different acrylic and methacrylic monomers.¹⁹ The anti-fog properties of UV-cured coating were measured by contact angle test and anti-fog test.¹⁹ The AMPS content in prepolymer had a great influence on the anti-fog properties of UV-cured coating.¹⁹ Figure 5.3 demonstrates anti-fogging performance of coating.

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REASONS FOR ODOR FORMATION IN PLASTIC MATERIALS

6.1 EFFECT OF POLYMER

The odor of plastics is a result of many different influences, mostly discussed in this chapter, but many references are included in other chapters as well. It is common to recognize that plastics emit odorous substances, but it is much less common to find information on polymer regarding components of its odor.

The tires are probably the most common example of odor emission from polymeric materials, but their odor composition is mostly due to the additives rather than to the polymer itself.

The odor comes from a chemical composition or it is derived from petroleum refining and composition of raw materials used in polymerization.¹ The raw polymers are often exposed to pressure, residence time, and temperature during their processing to form a commercial product (e.g., powder, granulate, etc.).¹ Ingredients present in the raw materials could react/degrade when subjected to these high temperatures and pressures, and give off chemicals or compounds not otherwise present in the raw materials.¹ The high temperatures and pressures could be the result of extrusion of polymer composition or its drying conditions.¹ These resulting chemicals and compounds might produce organoleptically-detectable odors.¹

Polyamide-66, which was not exposed to any thermal treatment with the exception of its production conditions, contains substantial concentrations of several volatile components, such as cyclopentanone, 2-ethyl-cyclopentanone, 2-pentyl-cyclopentanone, and 2-cyclopentyl-cyclopentanone.² Most of these components increase in concentration when polymer is exposed to the thermooxidative conditions, but cyclopentanone is found to decrease on the thermal oxidation.² This may mean that the original odor of polyamide-66 is modified by the conditions of processing (and can be even reduced).

In poly(ethylene terephthalate), acetaldehyde and 2-methyl-1,3-dioxalane are typical components of volatile materials causing odor.³ Both components are present in the packaging material which is to be subjected to γ -sterilization.³ 2-methyl-1,3-dioxalane concentration decreases on exposure to γ -radiation, whereas acetaldehyde concentration increases on exposure.³

In polypropylene, short chain hydrocarbons (alkanes, alkenes, and dialkenes) were found in the emitted compounds.⁴ If the chain was shorter than 16 carbon atoms, these compounds did not contribute to fogging, but participate in the smell formation.⁴

Table 6.1 gives information on the specific odor of different polymers as they were characterized in the Polymer Handbook.⁵

6.1. Typical polymer odors. [Data from Wypych G, **Handbook of Polymers**, 2nd Ed., *ChemTec Publishing*, Toronto, 2016.]

Polymer	Characteristic odor
Acrylonitrile-butadiene elastomer	slight rubbery
Bromobutyl rubber	none to mild
Carrageenan	slight marine
Cellulose acetate butyrate	slight, characteristic
Chlorobutyl rubber	mild
Ethylene n-butyl acrylate carbon monoxide terpolymer	mild acrylate-like
Ethylene-vinyl acetate copolymer	mild, ester-like
Gelatin	musty
Linear low density polyethylene	mild hydrocarbon
Poly(acrylic acid)	acetic
Poly(acrylonitrile-co-styrene-co-acrylate)	faint specific
cis-1,4-Polybutadiene	rubber-like
Poly(butyl methacrylate)	methacrylate
Polychloroprene	mild
Polyethylene, chlorosulfonated	slight, ether-like
Poly(ethyl acrylate-co-methyl methacrylate)	characteristic, faint
Poly(ethylene-co-acrylic acid)	acidic
Poly(ethylene-co-butyl acrylate)	characteristic, acrylic
Poly(ethylene-co-n-butyl acrylate)	faint acrylic odor
Poly(ethylene-co-ethyl acrylate)	characteristic, acrylate
Poly(ethylene-co-methacrylic acid)	mild methacrylic
Poly(ethylene-co-methyl acrylate)	ester-like
Poly(ethyl acrylate-co-methyl methacrylate-co-triammonoethyl methacrylate chloride)	characteristic, faint
Poly(methyl methacrylate-co-acrylonitrile-co-butadiene-co-styrene)	faint, specific
Polymethylsilsesquioxane	characteristic
Polynorbornene	characteristic
Polypropylene	acid (some)
Polypropylene glycol	sweet
Polypropylene, maleic anhydride modified	mild hydrocarbon
Poly(styrene-co- α -methylstyrene)	slight, hydrocarbon
Poly(styrene-co-butadiene-co-methyl methacrylate)	pungent, sweet
Poly(vinyl butyrate)	slightly pungent

6.1. Typical polymer odors. [Data from Wypych G, *Handbook of Polymers*, 2nd Ed., ChemTec Publishing, Toronto, 2016.]

Polymer	Characteristic odor
Poly(vinyl chloride-co-vinyl acetate)	mild, pleasant
Poly(N-vinyl pyrrolidone)	faint, specific
Silane-crosslinkable polyethylene	very faint
Styrene-butadiene block copolymer	faint, specific

Table 6.1 shows that many polymers (18% of those reported in the Handbook of Polymers)⁵ have a specific odor. In acrylic polymers, odor seems to come from unreacted monomers or perhaps low molecular fragments. Hydrocarbon polymers have the hydrocarbon-like odor, which also points to low molecular weight fragments. Rubbers have a rubbery odor (even if they are synthetic). Other polymers also seem to have odor related to their monomeric composition.

It would be very useful if these polymers were tested by GC/MS and compositions and concentrations of their volatiles were known, considering that odor is an essential factor of quality. It is known⁴ that polypropylene can be made odorless, therefore full awareness of composition of volatiles is an important quality factor, which can be considered in a specification.

Using gas chromatography, multivariate data analysis, and sensory methods, polypropylene and polyethylene were analyzed concerning composition of degradation products for stabilized and unstabilized polymers analyzed under air and nitrogen.⁶ In stabilized polypropylene, analyzed in the presence of air, acetaldehyde, acrolein, acetone, formic acid, 2-methyl pentane, methacrolein, acetic acid, 2,4-pentadione, 2,4-dimethyl hexane, 4-methyl octane, and 4-ethyl decane were detected.⁶ The following compounds were present when analysis was conducted under nitrogen (acrolein, acetone, 2-methyl pentane, methacrolein, acetic acid, 2,4-pentadione, 2,4-dimethyl hexane, 4-methyl octane and 4-ethyl decane).⁶ In the polyethylene, volatile products found under the air atmosphere were ethylene, n-hexane, acetic acid ethyl acetate, n-octane, 2-methyl octane, n-nonane, n-decane, n-dodecane, and n-tetradecane.⁶ All these compounds (and additionally furfural) were present when analysis was conducted under nitrogen.⁶ GC-MS did not detect odor-active compounds, which were detected by GC-olfactometry and detection frequency (SNIF) analyses.⁶ The odor-active substances are carbonyl compounds.⁶ The unsaturated ketones and aldehydes with six to nine carbon-atoms are the main odor drivers due to their low sensory threshold values.⁶ The unanswered question is when these oxidation reactions take place: during polymerization or are these compounds already present in the monomer feedstock?⁶

6.2 EFFECT OF ADDITIVES

Additives are essential odorants because they are usually low molecular substances which can migrate and/or evaporate at room temperatures.

Study of plasticizer TXIB (2,2,4-trimethyl-1,3-pentanediol diisobutyrate) and ethanol *via* olfaction and *via* ocular and nasal chemesthesis, i.e., chemically stimulated feel, shows another reason for the importance of additives in odor formation.⁷ Olfactory detec-

tion of TXIB began at concentrations below 1 ppb, with 50% correct detection at 1.2 ppb (comparable detection for ethanol occurred at almost two orders of magnitude higher.)⁷ Chemesthetic detection of TXIB began at about 500 ppb, with 50% correct detection at 2.1 ppm for the eye and 4.6 ppm for the nose, both close to saturated vapor concentration (comparable detection for ethanol occurred essentially three orders of magnitude higher.)⁷ This shows that plasticizers can be detected by olfactory and the chemesthetic detection at very low concentrations. Therefore, even though plasticizers have high evaporation temperatures and low vapor pressures, they can be detected by our senses. In addition, plasticizers can migrate to the surrounding liquids and solids in contact, making them even stronger odorants due to the chemesthetic detection.⁷

Plasticizers are not only added to polymers to make them softer but also used sometimes to protect polymers against photodegradation. Research has shown that synthetic materials such as PE and PEX are capable of leaching volatile organic compounds.⁸ These polymeric materials are frequently coated with plasticizers, antioxidants and application solvents that serve as radical scavengers that inhibit oxidation of the plastic pipe.⁸ One study assessed the odor from an unspecified PEX material using the quantitative standard threshold odor number, TON. TON higher than 5, which exceed the secondary maximum contaminant level (TON = 3), was observed for PEX pipes.⁸ Nonanal, decanal, butylbutanoate, xylene, 2-ethyl-1-hexanol 2,5-dimethyl-2,5-hexanediol and 2,2-diethoxypropane were found by solid-phase microextraction/gas chromatography/mass spectrometry.⁸

2-Ethyl-1-hexanol is linked to the common plasticizers, such as bis(2-ethylhexyl)adipate, bis(2-ethylhexyl)sebacate and bis(2-ethylhexyl)phthalate.¹⁴ In addition, PVC-based items containing these plasticizers emit 2-ethyl-1-hexanol.¹⁴

The odor of the drinking water was described by local people as "olive odor".⁹ The odor of a sample was described as green apple, fruity, and olive oil by panelists.⁹ GC/MS showed that the sample contained high levels of 2,4-di-tert-butylphenol, which is a degradation product of frequently used antioxidant.⁹

High density polyethylene, crosslinked polyethylene, and polyvinyl chloride pipes for drinking water were tested with respect to migration of volatile organic components to water.¹⁰ It was found that HDPE pipe causes the formation of odor because of migration of 2,4-di-tert-butylphenol, which is a known degradation product of antioxidants, such as Irgafos 168.¹⁰ Crosslinked polyethylene, PEX, also contributed to odor formation.¹⁰ 2-Ethoxy-2-methylpropane, ETBE, was identified as a contributor to the odor from the PEX pipe.⁸ Aqueous ETBE concentrations ranged from 23 to >100 µg/L in the leachate water.⁸ Panelists were able to smell ETBE at a concentration of 5 µg/L.⁹ In the case of PVC pipe some amounts of hexanal, octanal, nonanal and decanal were detected.¹⁰ The quantitative threshold odor number, TON, for PVC pipe was zero, unlike in the case of HDPE and PEX pipes, where TONs were higher than 5.¹⁰

Additives are not always contributors of odor, but in many cases they prevent odor formation, especially in the case of packaging materials for food. Use of TiO₂ tinted polystyrene with a layer containing aluminum oxide and carbon black protected contents (sour cream) from photodegradation.¹¹ In another study,¹² poly(ethylene terephthalate) film was used for packaging of pasteurized milk. When UV stabilizer was added, milk was effectively protected from UV degradation.¹²

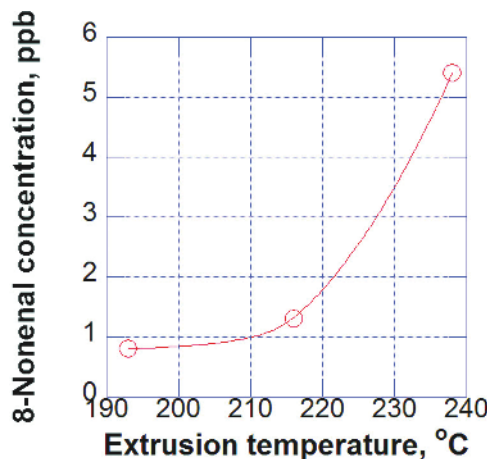


Figure 6.1. Effect of extrusion temperature on 8-nonenal concentration in HDPE samples. [Data from Sanders R A, Zyzak D V, Morsch T R, Zimmerman S P, Searles P M, Strothers M A, Eberhart B L, Woo A K, *J. Agric. Food Chem.*, **53**, 1713-16, 2005.]

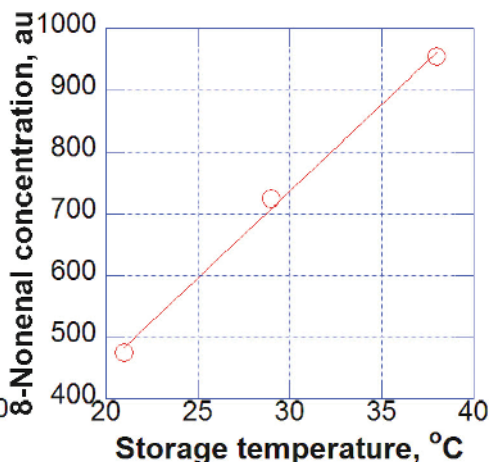


Figure 6.2. Effect of storage temperature on 8-nonenal concentration in corn chips stored in HDPE containers. [Data from Sanders R A, Zyzak D V, Morsch T R, Zimmerman S P, Searles P M, Strothers M A, Eberhart B L, Woo A K, *J. Agric. Food Chem.*, **53**, 1713-16, 2005.]

It was found in a patented invention that odor of additives can be easily corrected in the case of sulfurized phosphorous compounds by reacting phosphorous compounds with reactive sulfur sources before addition of polysulfides.¹³ This process permits production of lubricating additive which is odor free.¹³

The above are just a few examples of effects of additives on an odor of polymeric materials. More specific cases are discussed in Chapters 8 and 9.

6.3 EFFECT OF PROCESSING CONDITIONS

Food and beverage products stored in polyethylene containers may absorb some of their volatile components to acquire characteristic “plastic” odor.¹⁵ Nonenal is one of the major components of volatiles credited with influencing this “plastic” odor. Figure 6.1 shows that with extrusion temperature increasing, concentration of 8-nonenal in HDPE is increased.¹⁵ Concentration increase is accelerated by higher temperatures. Figure 6.2 shows the effect of storage temperature on concentration of 8-nonenal in corn chips stored in HDPE containers.¹⁵ Here concentration of 8-nonenal is a linear function of storage temperature.¹⁵ 8-Nonenal is a secondary product of oxidation of an alkyl diene (e.g., 1,9-dodecadiene) proceeding through a dodecenyl hydroperoxide intermediate.¹⁵ Dodecene is one of the most abundant components of HDPE volatiles.¹⁵ 8-Nonenal is the most important odor-causing component in both oxidized LDPE and oxidized HDPE.¹⁵

GC/MS thermal desorption system with simultaneous sniffing was used for determination of off-odor compounds and VOCs in fumes formed during extrusion coating of low-density polyethylene.¹⁶ A large number of aldehydes and ketones were identified as carbonyl compounds present in fumes.¹⁶ Particularly bad odors of ketones were caused by 2-pentanone (pungent and acrid odor), 3-heptanone (bad, sweet odor), butyrolactone (stale odor), and 7-octen-2-one (bad and stale odor).¹⁶ Significant odors also were caused by

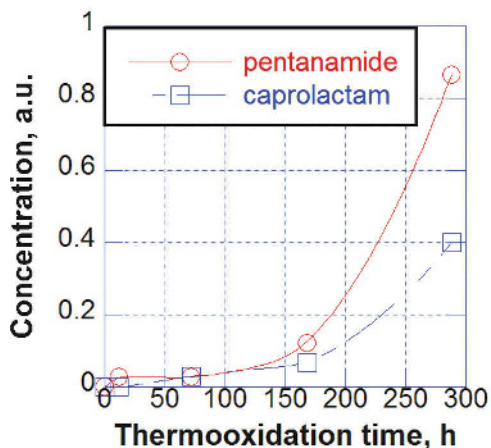


Figure 6.3. Concentration of pentanamide and caprolactam in products of thermooxidation of polyamide-66. [Data from Hoeglund A, Lindqvist A, Albertsson A-C, Berglund B, *Polym. Deg. Stab.*, **97**, 481-87, 2012.]

Some of the volatile compounds that produced negative odors in heated triolein, in order of increasing concentration, were hexanal (grassy), octanal (fruity), (E)-2-decenal (plastic), nonanal (fruity), and (E)-2-undecenal (plastic).¹⁷ Some of the odorous compounds in trilinolein heated for 1, 3 and 6 h, in order of increasing concentration, included (E)-2-nonenal (plastic), pentanal (grassy), and hexanal (grassy).¹⁷

Figure 6.3 shows the effect of thermooxidation time on volatiles produced from degradation of polyamide-66.² In total, fourteen different volatile compounds were detected in products of thermal degradation of polyamide-66.² Thermooxidation was conducted at 90°C.² The odor intensity correlated with a deterioration of tensile strength and the amount of degradation products released.² A 150% increase in odor intensity occurred concurrently with a significant deterioration in mechanical properties, and an increase in the amounts of a total of eight of the degradation products released from the polymer matrix.² Precision of the determination of volatiles permits us to use this method to predict construction failure of materials produced from polyamide-66.²

Typically alkanes, alkenes, and dialkenes dominate the volatiles obtained from polypropylene degradation.⁴ Emission depended on the sample surface rather than on sample mass.⁴ Emitted amount of volatiles depended on polypropylene grade.⁴

Hexanoic acid, acetic acid, 2-methoxyphenol, acetyl furan, diacetyl, and aldehydes were the most important odorants emitted during production of wood plastic composites based on polyethylene and its blend with EVA.²¹ The degradation of wood resulting from high processing temperatures may lead to undesirable odors.²²

It was shown in a patent that materials can be easily deodorized by heating under vacuum.¹⁸ This type of treatment was useful in removing volatiles from polyol.¹⁸ Hexanal, nonanal, and decanal were removed as odor components.¹⁸

Irradiation of packaging materials is a common technique of sterilization. It leads to a formation of free radicals and ions, with secondary effects such as crosslinking as well as oxidative chain scission.¹⁹ These effects result in a formation of volatile radiolysis products which may induce off-odors and may change the migration characteristics of packaging materials.¹⁹ Irradiation affects also polymer additives which change their specific migration behavior and additive related decomposition products.¹⁹ Figure 6.4 shows

some aldehydes such as butanal and decanal.¹⁶ In total, more than 200 compounds were identified in fumes collected during the extrusion coating of LDPE.¹⁶ Extrusion was conducted at 285 and 315°C.¹⁶ At higher extrusion temperature, more odorous compounds were produced.¹⁶

Thermal stability of triolein and trilinolein were studied to better understand the production of undesirable odors such as fruity, plastic, and waxy that are characteristic of higher oleic acid-containing oils.¹⁷ Some of the volatile compounds that produced negative odors in heated triolein, in order of increasing concentration, were hexanal (grassy), octanal (fruity), (E)-2-decenal (plastic), nonanal (fruity), and (E)-2-undecenal (plastic).¹⁷ Some of the odorous compounds in trilinolein heated for 1, 3 and 6 h, in order of increasing concentration, included (E)-2-nonenal (plastic), pentanal (grassy), and hexanal (grassy).¹⁷

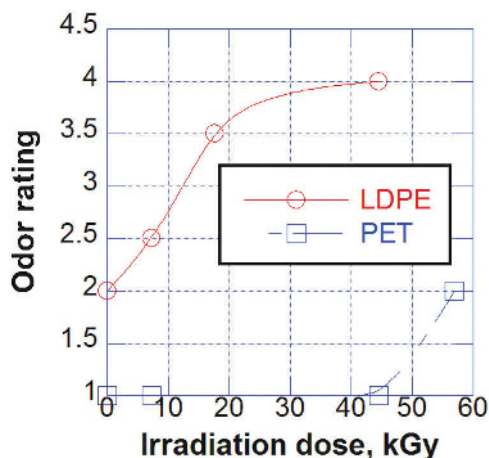


Figure 6.4. Odor rating of packaging materials vs. irradiation dose. [Data from Welle F, Mauer A, Franz R, *Radiat. Phys. Chem.*, **63**, 841-44, 2002.]

crosslinking effect of small doses of γ -irradiation (5–10 kGy) and the pronounced scission of the main chain at higher doses (30–200 kGy) by the cleavage of the weak carbonyl bond between the phenyl rings.²⁰

The volatile compounds released from 13 different multilayer polymeric materials for food use, before and after their exposure to gamma radiation, have been assessed by the solid-phase microextraction-gas chromatography-mass spectrometry.²³ 60-80 compounds were identified in each packaging film.²³ A peak of 1,3-ditertbutylbenzene was present in most of the irradiated samples.²³

Unsaturated slip additives have poor oxidative stability.²⁴ Their degradation products affect taste and odor of the polymer.²⁴ Incroslip SL is fully saturated with high oxidative stability, meaning that it will not degrade over time or after exposure to heat and UV light.²⁴ Oxidative stability is particularly important in application, such as caps for water bottles.²⁴

The amount of vinyl chloride extracted from PVC significantly increased from 8 to 18 ppm as the dose of irradiation increased to 200 kGy.²⁰ The dose-dependent formation of vinyl chloride in PVC could be due to the extensive main chain scission effect with increasing irradiation dose.²⁰ PVC sheet was very sensitive to γ -irradiation and the blue-colored sheet turned brown and released a strong off-odor.²⁰

6.4 RECYCLING

Recycled materials have already been processed. They, therefore, contain various products of thermal degradation. Some recycled materials have been exposed to environmental elements and they contain products of environmental degradation which may increase their thermal degradation rate on reprocessing.

Polymeric materials absorb volatiles from materials they have been in contact with, or in close proximity to them.²⁵ When detergents are stored in polyethylene bottles, for

the effect of γ -irradiation on odor in packaging materials.¹⁹

Polyamide-6, a food packaging polymer, was irradiated with a dose ranging 5–200 kGy.²⁰ The dose of γ -irradiation significantly increased the formation of ϵ -caprolactam in PA-6, ranging between 122 and 164 ppm in the dose range 5–200 kGy.²⁰

The low doses of γ -irradiation (5–10 kGy) did not significantly affect the bisphenol-A level in polycarbonate film.²⁰ But its level increased to 473 mg/g when the PC film was exposed to 30 kGy, and it did not change when higher doses were used (60, 100, and 200 kGy).²⁰ The increase in bisphenol-A level in PC film exposed to 30 kGy could be attributed to the predominant

example, the fragrances used in the soaps diffuse into plastic material and impart an odor.²⁵ This odor may be objectionable in other applications.²⁵

LDPE contains modifying agents such as antistatics which degrade under thermal reprocessing.²⁶ This results in significant odor emissions.²⁶ The extraction of used films and oil bottles can reduce the odor emissions to the level of new HDPE granulate.²⁶

Reprocessing of HDPE with different regrind levels affects concentration of 8-nonenal, which is known to produce odor.¹⁵ For example, canisters with typical regrind level contain 1.5 ppb of 8-nonenal (starting resin has 0.5 ppb).¹⁵ Canisters with high regrind level contain 2.0 ppb of 8-nonenal.¹⁵

Melting and powdering processes during the processing of plastic waste in waste recycling plants generate harmful gas emissions which have potentially adverse health impacts, not only on employees but also on nearby residents.²⁷ The concentration of the emissions from the PVC plastic waste recycling plants was higher than those from the PE/PP plastic recycling plants.²⁷ Organochlorinated compounds were measured in the ambient air emitted from the PVC plastic waste recycling plant. PE/PP plastic waste from recycling plant produced high concentrations of polycyclic aromatic hydrocarbons.²⁷ In a PVC recycling plant, a large number of volatile substances have been determined, which belong to chlorine-containing compounds, hydrocarbons, ketones, aldehydes, and others.²⁷ In PE/PP plastic waste plant large number of different emitted substances belonged to chlorine-containing compounds, hydrocarbons, ketones, esters, aldehydes, and others.²⁷

There are known methods of odor removal from recycled materials. These include contacting of recyclate with hot gas under vacuum,²⁵ stripping volatiles,²⁸ and addition of other substances.²⁹ Polyolefin chips were contacted with heated gas to produce material which was essentially free of odors and suitable for food contact applications.²⁵ Ethylene vinyl acetate copolymer was subjected to high-pressure recovery of unreacted ethylene and odor of acetic acid was also removed in the process.²⁷ Odor in HDPE was eliminated when some amounts of polyalkene imine, PAI, or polyethylene imine, PEI, were added in compounding extruder to HDPE waste and mixture was processed at suitable conditions as to produce granulate.²⁹

Volatile organic compounds, polycyclic aromatic hydrocarbons, and phthalate esters were analyzed in Xingtian Town, the largest distribution center of plastic waste recycling in China.³⁰ The total concentrations of volatile monocyclic aromatic hydrocarbons, polycyclic aromatic hydrocarbons, and phthalate esters ranged from 2000 to 3000 $\mu\text{g m}^{-3}$, 450 to 1200 ng m^{-3} , and 200 to 1200 ng m^{-3} , respectively.³⁰

6.5 CONTACT WITH OTHER MATERIALS

In the previous section, an example was given of polyolefins which are contacted with fragrance-containing products.²⁵ This example shows that plastic materials are capable of absorbing volatile substances, which change the odor characteristics of polymer because of participation of fragrances and their degradation products in the formation of characteristic odor.

Silane-crosslinked polyethylene, PEX, pipes produce characteristic odor in drinking water.⁸ The presence of disinfectant, chlorine or chloramines in drinking water did not alter the odor characteristics or intensity of the PEX odor.⁸ The chemical/solvent odor was rated higher when the chlorine concentration was low.⁸ No chlorinous odor was detected

when monochloramine was used, even though chemical analysis showed chloramines present.⁸ Monochloramine odor, therefore, did not mask the 2-ethoxy-2-methylpropane (major odorant in the case PEX pipe) odor.⁸

High-density PE containers had imparted “plastic” odor to an experimental corn chip product.¹⁵ This is typical of many food products which are packaged in plastic packaging. Figure 6.2 shows that the storage temperature is a factor in the accumulation of odorants in food products in contact with volatile-containing plastic packaging.

6.6 EFFECT OF STORAGE CONDITIONS

Effect of storage conditions on formation of odor is a commonly known phenomenon. Contact or proximity of other materials only differ by the rate of volatile absorption but materials in proximity also form an environment in which products in the neighborhood become contaminated. Also, selection of products for storage in the same place has a profound effect on odor transmission.

Volatiles associated with confinement odor (3-methyl-butanal, 3-hydroxy-2-butanone and sulphur dioxide) corresponded with end/sub products of glucose fermentation and catabolism of amino acids by bacteria (all bacteria naturally found in meat and do not represent a risk to health)³¹. Confinement odor indicates a stage at which the environment for bacteria growth is becoming favorable for the production of volatiles with strong odors that are noticed by the consumer.³¹

6.7 EFFECT OF HUMIDITY

The effect of air humidification on the perception of indoor air quality in-office workers was analyzed.³² It was found that the perception of stuffy air increased as humidification increased from 30% to 40%.³²

Relative humidity did not affect source emissions, but increased relative humidity could enhance the human perception of odors.³² The following relationship was proposed which related odor concentration to relative humidity:³²

$$\log C_{ou} = 1.588 + 0.525 \times \log (C_{H_2S} + C_{DMS} + C_{DMDS}) + 0.01 RH \quad [6.1]$$

where:

C_{ou}	odor concentration
C_{H_2S}	concentration of H_2S in ppmv
C_{DMS}	concentration of dimethyl sulfide in ppmv
C_{DMDS}	concentration of dimethyl disulfide in ppmv
RH	relative humidity

Relative humidity, as an independent variable, significantly enhances the ability of investigators to associate odors with odorants because it affects the odor acuity of the exposed individuals.³²

Indoor air temperature and humidity may be important for the perceived air quality and sick building syndrome symptoms.^{33,36} Perceived indoor environments, nonspecific symptoms, and their associations are affected by season.³³

Both the temperature and the relative humidity affected the emission rates but depended strongly on the type of building product and the type of volatile component.³⁴ Some odorants such as 2-ethylhexanol, dimethyloctanol, and 1,2-propanediol were evapo-

rating faster from carpet, sealant, and wall paint, respectively, when relative humidity was increased, but much other volatiles, especially high boiling liquids, were not affected by relative humidity.³⁴

Humidity and temperature usually influence a quartz crystal microbalance gas sensor response.³⁵ Not only the magnitude of sensor response but also the response speed explicitly changes.³⁵ When the humidity increases, the magnitude of odor reading gets smaller and the response speed becomes slower.³⁵ When the temperature increases, the magnitude becomes larger and the response speed becomes faster.³⁵ It is noticeable that the effect of temperature follows a trend experienced by human testers but the humidity trend is opposite to that of human perception. It is, therefore, essential to apply proper humidity correction.

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METHODS OF TESTING IN ODOR ANALYSIS

7.1 MECHANISM OF SMELL

Mechanism of smell is best explained today by electrochemical theory, which consists of several elements discussed in a sequence below. Compounds which do not form dipoles do not have odor.¹ Examples include hydrogen, nitrogen, and oxygen.¹ Alkanes have no or small dipole moment (e.g., methane 0, ethylene 0, or propane 0.08) and they have a relatively weak odor.¹ Alcohols have the considerable dipole moment (e.g., methanol 1.70, ethanol 1.69, or 1-propanol 1.68) and they have a moderate odor. Aldehydes have high dipole moment values (e.g., formaldehyde 2.33, propynal 2.47, propanal 2.52, or propenal (acrolein) 3.12) as do ketones (acetone 2.88 or diketene 3.53), acids (formic acid 1.41, acetic acid 1.74, or propanoic acid 1.75), esters (methyl acetate 1.72, ethyl acetate 1.78, or ethyl formate 1.93), amides (formamide 3.73), and nitriles (hydrogen cyanide 2.98, acetonitrile 3.90, or propionitrile 4.02) and they usually have strong odors. Polarity of a compound gives some crude indication of its odor but there is limited correlation between dipole moment and odor strength.¹

It is therefore suggested that since odorant dipole moments do not correlate with odor strength, then perhaps interaction of dipole forces of odorant with dipole forces of smell receptors (protein of a particular chemical composition) explain observed odor by the sense of smell.¹ In addition to chemical structures of both odorant and receptor, some modifications may also occur because of interactions of dipoles or ions in the receptor, hydrogen bonding, ion formation with volatile acids and bases, and covalent bonding.¹ For these reasons odorants with similar dipole moments may have different odor strength when binding to different receptors.¹ This information should be compared with the discussion of smell and taste receptors in Chapters 3 and 4. It should be noticed from this comparison that one receptor can recognize multiple odorants but also that one odorant can be recognized by multiple receptors. Therefore, different odorants are recognized by different combinations of receptors.¹ This means that the olfactory system uses a combinatorial receptor coding scheme to encode odor identities, therefore slight changes in an odorants composition or its concentration may alter its code.¹

The next step is conveying the message of the established code to the center of decision making (the brain). In the first step of this action, receptor ligand interacts with olfactory neurons.¹ Electrical potentials are formed in neurons from ion gradients, and these electrical impulses are carried along the axons (see Figure 3.1) by passing them from neuron to neuron.¹ The weak signals are sufficient to have a dramatic effect on specific pro-

teins in the axon membrane, which is called voltage-gated ion channels.¹ Membrane charge becomes more positive, or depolarizes, and the signal travels down the axon of the olfactory receptor cells to the olfactory nerve.¹ Due to this electrochemical activity, the brain obtains sensory input from the olfactory bulb through the cerebral olfactory cortex.¹ Signal transduction involves electrochemical effects.¹ It is supposed that calcium-gated chloride channels are activated during odorant detection in the chemosensory membrane of olfactory sensory neurons during signal transduction.¹

More extensive treatment of the subject can be found elsewhere.¹ Here, we have only discussed the framework of changes leading to the acquisition of the signal and its transmission to the brain to realize the odor. It shows the extreme complexity with which human-made instruments for odor-sensing must compete in order to become useful tools in odor recognition. The above short discussion and the previous chapter show many difficulties which can be expected in the operation of various methods of odor-sensing because of lack of direct correlation between properties of odorants and their odor characteristics and also influences of a combination of odorants, their concentrations, temperature, humidity, and sampling on a reading of resultant output.

It is interesting to note some information on the mechanism of smell loss. In the USA, about 500,000 patients have congenital loss of smell.² Out of this, 12% patients have Type I anosmia (hyposmia is a reduced ability to detect odors; anosmia is a condition in which no odors can be detected).² These patients know history of smell loss, have multiple defined congenital defects of brain, have multiple brain abnormalities of the olfactory system, have multiple somatic abnormalities involving several organ systems, and they are unable to recognize any external odor since birth.² The type II patients (remaining 88% of the group) do not know why they suddenly lost sense of smell.² The anatomy of the olfactory system in their brain exhibits some changes but they all have olfactory bulbs and olfactory anatomy consistent with a functioning olfactory system.² These patients are as unable to recognize any external odor similar to Type I patients.² Type I patients cannot be cured because they have permanent anatomical abnormalities in their olfactory system but 63% of Type II patients can begin to smell external odors after use of the phosphodiesterase inhibitor theophylline.²

7.2 SAMPLING

Selection of proper sampling methods determines the accuracy of results. The following major principles of sampling should be fulfilled:³

- no impact on the characteristics of the source
- representativeness of the source emission
- no influence on the sample with equipment used

To get representative and reproducible results, the sampling technique must be selected respective of the type of odor source, which belongs to one of the group, as follows:³

- point
- line
- area
- mobile

Point source emits in a localized, restricted area (e.g., open gas collector); line source emits in elongated fashion (e.g., long cracks); area sources usually cover a large surface area (e.g., biofilters for cleaning exhaust gases or landfill sites); mobile sources change their position (e.g., automotive equipment).³

In addition to the above division, emission sources are divided into active and passive.³ Active means that there is outward airflow (e.g., composting piles with forced aeration).

Depending on the above characteristics, the selection of an odor sampling device may influence the composition of the resulting odor sample.⁴ Sampling practice should, therefore, be based on the fundamental physical and chemical principles, the nature of the odor source, and the conditions created by the sampling device.⁴

Estimation of the emission rate from the area sources is done, either by⁴

- indirect measurement (it is based on a micrometeorological method, in which emission rate is derived from the measurement of wind velocity and concentrations across the plume profile downwind of the source)
- direct measurement (using some sort of enclosure, e.g., hood, chamber, or tunnel; the data on the concentration of compounds of interest in samples obtained from the device are combined with the data on the physical dimensions of the device and operating conditions. They both require calculation of the emission rates)

The first method does not affect the emission process because a sampling device is not used, but a large number of samples required to characterize the emitted plum make this method impractical in use for the odor determination.⁴

The following physical and chemical considerations have to be applied to selection of sampling method:⁴

- composition of the sample
- the implication of Henry's law constant
- influence of water and air temperature
- influence of wind velocity
- influence of water velocity (turbulence)
- influence of surface contamination
- influence of chemical reactions

The odor is usually caused by a composition of many chemical substances. In some investigations, 330 different chemicals were identified from an odor source.⁴ Not all of the chemicals are equally odorous, i.e., odor detection and recognition thresholds vary considerably (see Section 7.1).⁴ Sampling method should not change proportions between components of the mixture.⁴ A collection of samples with a cold-trap isolated a different range of chemicals than sorbent-based sampling technique.⁴

Frequently odor samples are emitted from a pool of liquid or solid. In this case, volatile substances are partitioned between source and surrounding air based on their physical properties, described by Henry's law:

$$p = k_H c \quad [7.1]$$

where:

p	partial pressure of emitted substance in solution
c	concentration of emitted substance in solution
k_H	Henry's law constant

It should be noted that the value of Henry's law coefficient depends on temperature.⁴ Also, considering that emitted substance must diffuse through water and air boundary layers, the rate of air flow affects partition.⁴ Use of a device with unnaturally low air turbulence might favor the selection of odorants with large values of Henry's law constant.⁴

Water temperature determines the viscosity of the solution and molecular diffusivity of an emitted compound.⁴ The impact that temperature dependence of the Henry coefficient has on emission may be greater than the effect of other factors such as wind speed or turbulence.⁴ The liquid temperature has a greater influence on the emission rates than does the air temperature, which can effectively be ignored provided, it does not alter the sample composition after collection.⁴

Volatilization rates correlate with wind speed.⁴ The influence of wind velocity on the rates of emission for a range of organic chemicals has been experimentally determined.⁴ For example, the overall transfer coefficient of benzene (benzene/water solution) increased by a factor of four as wind speed was increased from 0 to 6 m/s.⁴

It was demonstrated for highly volatile chemicals with large dimensionless Henry coefficients that the emission rate was dependent on liquid turbulence induced by a stirrer, once a threshold power input was exceeded.⁴ This effect is more significant than that caused by increasing wind speed across the liquid surface.⁴ As wind speed (turbulence) within the sampling device increases, emission rates for compounds with large values of Henry's constant increase, but emission rates of compounds with small values of Henry's increase even more.⁴

Films on water surfaces (e.g., biofilms or hydrocarbon layers) create an additional transport obstacle, which is proportional to the thickness of the film.⁴ They also modify the hydrodynamics at the water surface by damping surface fluctuations.⁴

The emission of odor substances is influenced by chemical reactions (e.g., dissociation, hydrogen bonding, covalent reactions, etc.).⁴ Chemical reactions change an effective concentration of the chemical compounds in the liquid boundary layer.⁴

Sampling devices of different shape, size, and operating condition have been used to collect air samples and to determine rates of emission of volatile substances, including odor.⁵ Several problems are associated with the use of static and dynamic emission chambers, but the more turbulent devices such as wind tunnels do not appear to be subject to these problems.⁵

Static chambers are more likely to be circular than rectangular (8 of 27 cylindrical devices were static, while 5 of 65 rectangular devices were static).⁵ Dynamic devices are more likely to have a rectangular than cylindrical shape (19 of 76 dynamic devices were cylindrical, whereas 57 were rectangular).⁵

Samples from rectangular chambers were less concentrated than samples from cylindrical chambers because of the dilution by the much larger flushing rates.⁵

The US EPA dynamic emission chamber was developed to create a standardized method for measuring the emission of industrial chemicals from contaminated soils and liquid storage facilities.⁵ Samples collected by Compendium Method TO-15 are analyzed by GC/MS to determine toxic organic compounds in ambient air.⁶ This method is used in several ASTM standards including D1356, D5466, E260, and E355. The method documents sampling and analytical procedures for the measurement of subsets of the 97 volatile organic compounds.⁶ The atmosphere is sampled by the introduction of air into a



Figure 7.1. CDS30 Odor sampling device. [Adapted, by permission, from Olfasense GmbH, Germany].

pecially-prepared stainless steel canister.⁶ Both subatmospheric pressure and pressurized sampling modes use an initially evacuated canister.⁶ A pump ventilated sampling line is used during sample collection with most commercially available samplers.⁶ Pressurized sampling requires an additional pump to provide positive pressure to the sample canister.⁶ A sample of air is drawn through a sampling train comprised of components that regulate the rate and duration of sampling into the pre-evacuated and passivated canister.⁶ The average recovery rates reported for the 40 test industrial chemicals was 104%.⁵

The development of a wind tunnel by researchers at the University of New South Wales was a result of the requirement to create a device with well defined aerodynamic characteristics and assuring the consistent relationship between tunnel wind velocity and odor emission rate.⁵

Much effort has been undertaken in Europe to standardize the determination of odor concentration.³ DIN EN 13725 (2003) was developed as a practical guideline.⁷ The sampling, which affects enormously the result of olfactometry, is still not standardized in Europe.³ According to VDI 3475⁸ and VDI 3477,⁹ a hood is used for sample collection on active area sources.³ Also, a wind tunnel with defined flow rate of odorless air is used for sampling in Europe.³

Figure 7.1 shows CDS30 sampling device for collecting air (odor) samples in gas sampling bags. The materials that are in contact with the sample flow are PTFE and stainless steel, in compliance with EN 13725.⁷

In a landfill, nine sampling points were placed and 35 types of odorous substances were measured and quantified.¹⁰ The sampling points were in landfill tipping areas, gas extraction wells, leachate storage pool, leachate disposal pool, sludge discharge area, sludge disposal workplace, sludge sun drying site, and sludge landfill site.¹⁰ Two parallel samples were collected at each sampling point.¹⁰ Tedlar bags were placed in a vacuum-generating container.¹⁰ Using a vacuum pump connected to the container, 5 liters of the gas sample were drawn directly into the Tedlar bag *via* Teflon tubing with a 5 mm outside diameter inserted into the vent system.¹⁰ Ambient air samples were pre-concentrated by cryogenic liquid nitrogen according to a method described elsewhere.⁶ For aldehydes and ketones, commercial cartridges were used to collect the air samples.¹⁰ Colorimetric tubes were used to detect ammonia in the field.¹⁰ The main odorous substances emitted from the landfill site were styrene, toluene, xylene, acetone, methanol, n-butanone, n-butylaldehyde, acetic acid, dimethyl sulfide, dimethyl disulfide, and ammonia.¹⁰ But these varied depending on collection point, for example, the typical odorants in gas extraction wells were acetaldehyde, ethyl benzene, xylene, methylamine and dimethyl formamide, the typical odorants in sludge discharge area were methyl mercaptan, valeric acid, and isovaleric acid, while those in sludge disposal workplace were carbon disulfide, acetone, 3-pen-

tanone, methanol, and trimethylamine, and the typical odorants in other sampling points were hydrogen sulfide, n-butylaldehyde, and acetic acid.¹⁰

Concentrations of volatile organic compounds, including formaldehyde, in classrooms, kindergartens, and outdoor playgrounds of three primary schools were measured in spring, winter, and fall.¹¹ Active sampling was used for VOCs¹² and formaldehyde¹³ using Tenax TA (sample tubes were analyzed by an automated short-path thermal desorption/cryofocusing system) and 2,4-dinitrophenylhydrazine tubes, respectively. Formaldehyde requires different sampling and analysis procedures than other VOCs.¹¹ Full description of sampling methods can be found in EPA original documents.^{12,13} Higher VOC concentrations were measured indoors than outdoors.¹¹ Seasonal and spatial variations of the most abundant species were not significant, pointing at dominant indoor sources.¹¹

The odor is one of the most important problems for waste management plants.¹⁴ The analytical difficulties in odor measurements are related to the high number of volatile components, especially when concentrations are lower than their detection limits.¹⁴ The compounds are sampled with thermal desorbable radial diffusive samplers with Radiello-containing Tenax cartridges.¹⁴ The diffusive samplers offer numerous advantages such as simplicity and rapidity of analysis, low cost, and weight.¹⁴ The sampling system is made up of a cylindrical adsorbing cartridge (stainless steel cylinder) placed coaxially inside a cylindrical diffusive body made up of polycarbonate and microporous polyethylene.¹⁴ The cartridge holds 250 mg of Tenax (TA 20-35 mesh).¹⁴ The relative standard deviations for repeated samples and the recovery percentage were, respectively, less than 7% and about 97% for all compounds.¹⁴ The diffusive sampling method with thermal desorption permitted characterization of odor compounds emitted from a solid waste landfill with high repeatability.¹⁴ The measurements showed a good linearity of sampling; there was no systematic difference according to the collection period.¹⁴

A complex relationship between odor emission rates provided by the US EPA dynamic emission chamber and the University of New South Wales wind tunnel was determined.¹⁵ Emission rates derived from the wind tunnel and flux chamber are a function of the solubility of the materials being emitted, the concentrations of the materials within the liquid, and the aerodynamic conditions within the device.¹ The ratio of wind tunnel to flux chamber odor emission rates ranged from about 60:1 to 112:1 (the emission rates of the model odorants varied from about 40:1 to over 600:1).¹⁵

A review paper¹⁶ includes discussion of odor sampling regulations and the equipment used, as well as the mathematical considerations to be applied to obtain the odor emission rate for the sampled source typology.

7.3 ACTIVE ODOR SENSING

A conventional sensor works passively to convert physical or chemical quantities into electrical signals.¹⁷ It detects, recognizes, and makes a judgment, passing information in only one direction.¹⁷ Active odor sensing participates in the exploration of behavior prior to detection and recognition.¹⁷ A typical example of active chemical sensing is the use of an odor-source localization system in which the sensing system is exploring an object in actual space.¹⁷ The fundamental strategy for odor-source localization is to use the gas concentration gradient.¹⁷

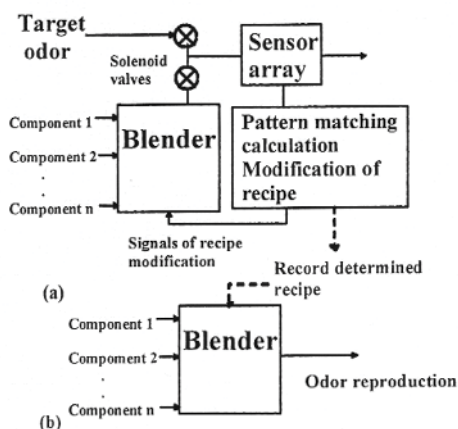


Figure 7.2. Principle of odor recorder. (a) recipe determination, (b) odor reproduction. [Adapted, by permission, from Nakamoto T, Nakahira Y, Hiramitsu H, Moriizumi T, *Sensors Actuators*, **B76**, 465-69, 2001.]

operation of the odor recorder can be found elsewhere.^{17,19}

Using the above method, apple flavor was reconstructed.¹⁸ The recipe contains basic components, including butyl isobutyrate, 1-butanol, 1-hexanol, propionic acid, and butyl propionate.¹⁸ The second formulation containing trans-2-hexenyl acetate, trans-2-hexenal, isobutyric acid, and ethyl valerate can be used to express differences in maturity.¹⁸ Several recipes for apples were reproduced and it was confirmed by a test panel that the reproduced apple flavors were the same as original.¹⁸

7.4 ELECTRONIC NOSE

An electronic nose is based on sensor arrays.²⁰ These arrays of sensors rely on²⁰

- the abilities of individual sensors to generate output by combining contributions from latent variables of odors
- the efficiency of data processing methods to build a parametric representation of the measured array responses in such a way that individual odor types (or classes) are associated with distinctly different sets of values of these parameters.

The parameters are mathematical descriptors of the odor identities, whereas the sets of their values specific to the different odor classes represent their mathematical signature.²⁰ They are referred to as feature vector, odorprint or chemical fingerprint.²⁰ The individual sensors in the array are chosen to provide varying degrees of cross-sensitivities for different chemical constituents in odors.²⁰ The set of sensor array outputs corresponding to an odor sample thus constitutes varied realizations of intrinsic variables of the odor identification.²⁰ Typical sensors include conducting polymers, metal oxide semiconductors, metal oxide semiconductor field effect transistor, piezoelectric (surface acoustic wave), optical fluorescence, quartz crystal microbalance, and amperometric gas sensors. A closer look at different sensors is available in Section 7.10.

Another example of the active odor sensing system is to use a preconcentrator.¹⁷ A preconcentrator is typically used to compensate for the sensor sensitivity.¹⁷

An odor recorder has been built based on the active odor sensing principle.¹⁷ It is an instrument capable of recording and reproducing smell.¹⁷ Figure 7.2 explains the principle of operation of the odor recorder. Recipe of original and reproduced odor must agree.¹⁸ A target odor is introduced into the sensor and its pattern is memorized.¹⁸ The odor from a blender is exposed to the sensor and its pattern is measured.¹⁸ The recipe of blended odor is modified until its pattern matches the pattern of original odor, after which the recipe is recorded.¹⁸ Odor from the recorded recipe can be reproduced.¹⁸ Details of the

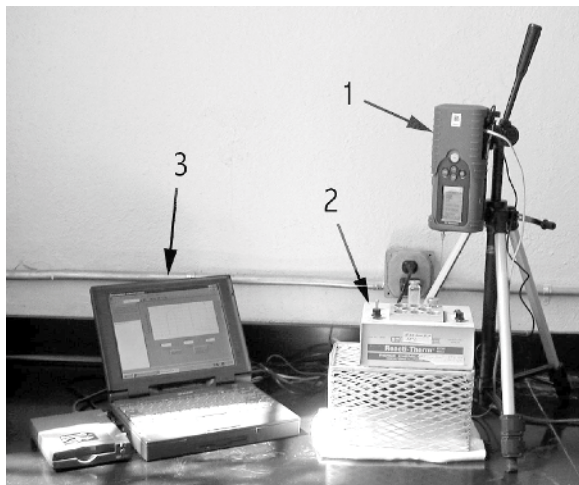


Figure 7.3. Cyrano Sciences Cyranose 320 workstation.
1) Cyranose 320, 2) sample heating block, 3) controlling computer.
[Adapted, by permission, from van Deventer D, Mallikarjunan P, *J. Food Sci.*, **67**, 8, 3170-83, 2002.]

Detection process includes the following steps: raw measurement, pre-processing, feature extraction, pattern recognition, classification, and decision-making process.²¹ The feature extraction process reduces the dimensional space of measurement to a lower volume of datasets.²¹ Pattern recognition helps to assign odor to a specific feature vector.²¹ Classification identifies an unknown sample as one from a set of previously learned odorants.²¹ Learning rules for odor recognition in an electronic nose and detailed method of data classification from the electronic nose can be found elsewhere.²²

Figure 7.3 shows the experimental setup of a workstation using electronic nose for odor detection. Figure 7.4 shows the close view of Cyranose 320 electronic nose. According to the manufacturer, the Cyranose 320 can be best thought of as a chemical vapor comparator. The instrument is first trained to recognize a series of chemical vapors or classes by creating a digital image or “smellprint” of each vapor. When challenged again with an unknown sample, the instrument digitizes and then compares this new smellprint to those stored in its memory. The instrument’s response is based on the summation of the chemical and physical properties of the entire sample and it is not intended to provide information concerning the composition of complex mixtures. The measurement is based on a change in the resistance of each chemical sensor in the 32-sensor NoseChip when exposed to a chemical vapor. This is a differential measurement of the sensor response measured as $(R_{\max} - R_0) / R_0$, with R_0 being the resistance during a baseline gas flow and R_{\max} being the maximum resistance during exposure to the sample vapor.

Figure 7.5 shows another commercial electronic nose system. It was developed for operation in the hostile industrial environments. The PEN, also called E-Nose, is small,



Figure 7.4. Cyranose 320.
[Courtesy of Intelligent Optical Systems, Inc., Torrance, CA, USA.]

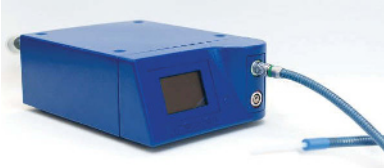


Figure 7.5. PEN industrial process control electronic nose. [Courtesy of Airsense Analysetechnik GmbH, Schwerin, Germany.]

fast and robust identification system for gases and gas mixtures. The detection of the gases is performed with an array of gas sensors. Single compounds or mixtures of gases can be identified, after a training stage, by using the pattern generated from the sensors. Using various algorithms, the instrument is able to identify up to 10 different compounds, or provides a straightforward answer like "Good-Bad", "Yes-No" depending on the needs of the user. The instrument can also deliver a quantitative statement.

One advantage of this technique is that the sensitivity to organic compounds can be increased by some orders of magnitude (detection limits in the low ppb range). These electronic noses are developed for application in food, materials, environment & safety, and medicine.

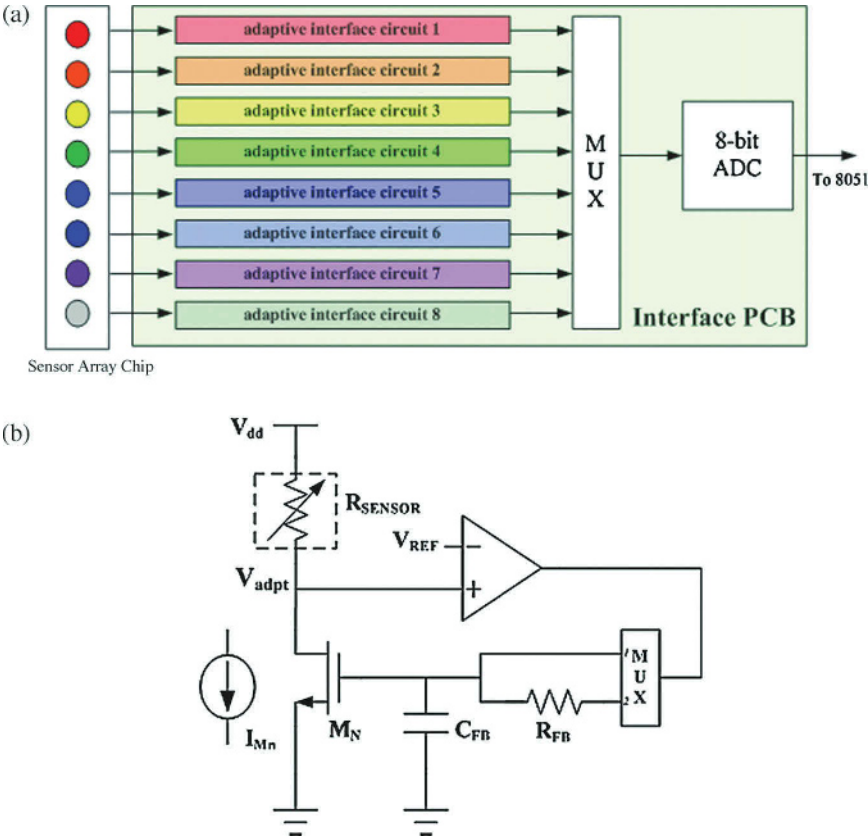


Figure 7.6. (a) Block diagram of the interface printed circuit board, and (b) schematic of the adaptive interface circuit. [Adapted, by permission, from Wang L C, Tang K T, Chiu S W, Yang S R, Kuo C T, *Biosensors Bioelectronics*, 26, 4301-7, 2011.]

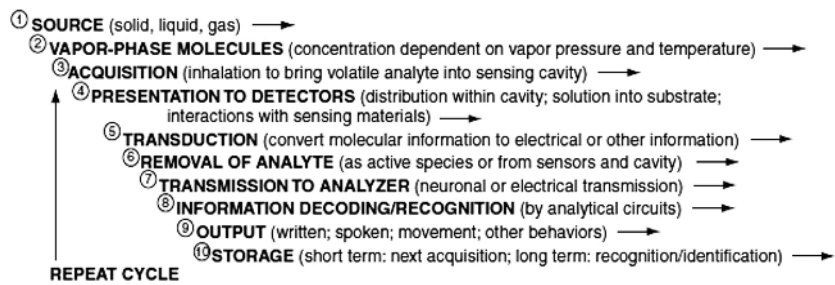


Figure 7.7. Steps in detecting vapor-phase compounds in the environment: encoding their molecular information by a detection system, recognizing the vapor-phase signatures, storing the results, and resetting the system for another detection event. [Adapted, by permission, from Kauer J S, White J, in **Electronic Nose, Encyclopedia of Neuroscience**, Elsevier, 2009, pp. 871-77.]

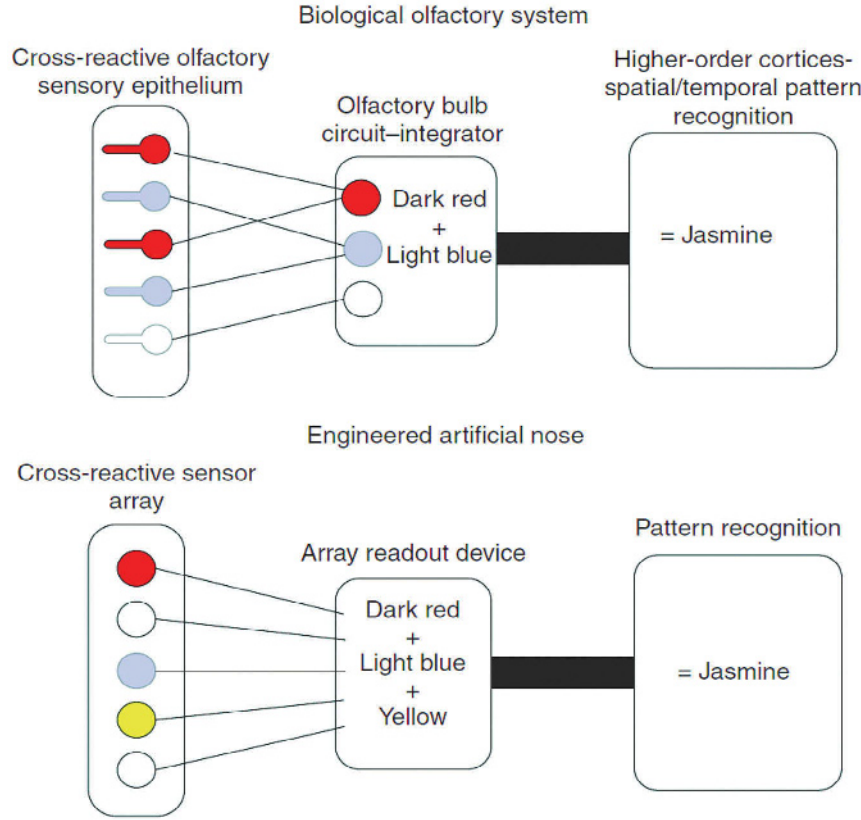


Figure 7.8. Schematic diagrams of the major components of biological and artificial olfactory systems: cross-reactive receptors or sensors, integration levels that receive the spatially and temporally distributed outputs from the sensor layer, and a pattern recognition level that categorizes, compares with stored information, and ultimately carries out identification. [Adapted, by permission, from Kauer J S, White J, in **Electronic Nose, Encyclopedia of Neuroscience**, Elsevier, 2009, pp. 871-77.]

Figure 7.6 shows a block diagram of the interface printed circuit board and schematic of the adaptive interface circuit.²⁴ Integrated printed circuit board interface (Figure

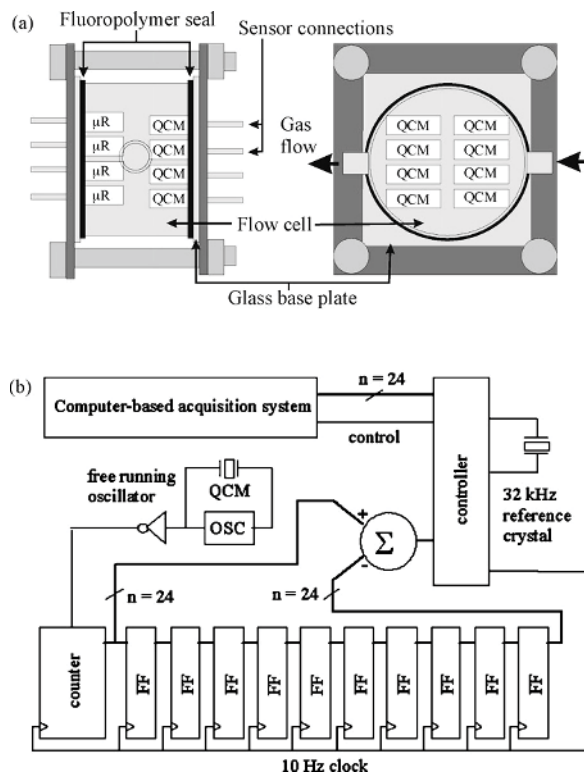


Figure 7.9. (a) The detector flow cell containing an array of 16 polymer-coated vapor sensors in a three-layer structure, where 8 pairs of complementary quartz crystal microbalance and resistor sensors face one another. The diagram shows (left) the side and (right) the plan views of the cell (in the plan view, only one set of sensors is shown). (b) Schematic diagram of the frequency acquisition, application-specific integrated circuit. [Adapted, by permission, from Mills C A, Beeley J, Wyse C, Cumming D R S, Glidle A, Cooper J M, *Sensors Actuators*, **B125**, 85-91, 2007.]

7.6a) has eight adaptive interface circuits, an eight-to-one multiplexer, and an 8-bit analog-to-digital converter.²⁴ The interface printed circuit board forms a bridge between the eight-channel sensor array chip and the microprocessor.²⁴ The eight adaptive interface circuits connect with eight different sensors.²⁴ Figure 7.6b shows the schematic diagram of the adaptive interface circuit.²⁴ The circuit has two operating modes. Mode-1 is a calibration mode. In this mode, prior to sensing odors, the multiplexer, MUX, chooses path “1” to charge the capacitor and control the gate voltage of transistor M_N .²⁴ This forces the voltage, V_{adpt} , to become equal the reference voltage, V_{REF} as a baseline signal.²⁴ Mode-2 is odor-sensing mode.²⁴ To sense odors, the MUX chooses path “0”.²⁴ In this mode, the sensor resistance change converts to a voltage change of V_{adpt} by Ohm’s law.²⁴

Artificial noses use biological principles to capture odor information.²⁵ The essence of all sensing systems is to convert different forms of sensory information

in the external world (visual, auditory, mechanical, chemical) into information encoded by the biological world of neuronal circuits in the brain or by the electronic circuits of the biomimetic system.²⁵ Figure 7.7 shows typical steps of measurement.²⁵ Figure 7.8 shows that there is a high similarity between a biological olfactory system and artificial nose in sensing and pattern recognition of odors.²⁵ The second essential element of electronic nose design is analytical.²⁵ Algorithms have been developed to associate the patterned output arising from the sensor arrays with the applied odorous analytes.²⁵ In most cases, recognition is carried out by a process that compares the input pattern from the test analyte with patterns that have been stored in computer memory during “training” sessions.²⁵ Identification can be compromised by the difficulties of differences in training/test analyte concentrations, the presence of interferent odorants that were not included during training sessions, and changes in temperature and relative humidity.²⁵

Figure 7.9 shows details of the flow cell and schematic diagram of the frequency acquisition.²⁶ The apparatus consists of a gas pumping system, a detector flow cell and detector electronics interfaced to a controlling personal computer.²⁶ The flow system was constructed mainly from glass to reduce absorption of odorant.²⁶

The noise removal is done by truncating the singular value of decomposition matrices up to a few largest singular value components, and then reconstructing a denoised data matrix by using the remaining singular vectors.²⁰ In the electronic nose systems, this method seems to be very effective in reducing noise components arising from both the odor sampling and delivery system and the sensors electronics.²⁰ This system is beneficial for improving classification efficiency of electronic noses by reducing overlap between classes in feature space.²⁰

The mapping between two electronic noses has been presented.²⁷ Mapping is a model that predicts the response of one electronic nose based on the response of the other.²⁷ Mapping is important for odor communication and synthesis, as well as for electronic nose data integration.²⁷

Electronic noses have found the following applications:²¹

- environmental control (air quality, pollutants, gas emission levels in factories, and chemical plant monitoring)
- medical (urine, skin, breathe odor analysis,³⁴ ulcer monitoring,³³ bacterial detection)
- food (coffee,³⁶ tea,³⁵ soft drinks, fish, meat, wine aroma control, fermentation process, identification of the bacterial organism, the progress of spoilage, quality control of fruits, development of food aroma composition, contamination by packaging materials)
- cosmetics (development of aroma formulation in perfumes)
- defense and security (land mines)
- pharmaceutical and chemical industries (measurement of odor, quality control, selection of raw materials, selection of polymer grade)
- automotive industry (testing raw materials for their odor emission)
- semiconductors (manufacturing process control)

Electronic noses have found many applications because they are simple, have broad sensitivity, are relatively inexpensive, can be small and portable, and are easy to train for improvement of detection.²⁵ They also have weaknesses, such as the influence of humidity and temperature on reading, need for frequent calibration, need for specially developed algorithms for a particular detection task, and lack of identification performance.²⁵

Figure 7.10 shows Scentroid SC300 a mobile olfactometer that is capable of odor measurement and analysis to international olfactometry standards: EN13725:2003, ASTM E679-04(2011), NVN2820, VDI 3881, GB/T14675-93. It can be transported to a site and deployed in minutes for a complete accredited olfactometric laboratory.

Below are some application examples of electronic noses recently available in the literature.

The electronic nose was used for monitoring the effect of mechanical damage of blueberries on their storage.²⁸ Blueberries were subjected to a repeated impact to determine changes in their volatile characteristics.²⁸ Various batches of blueberries were then stored at 2°C and 95% relative humidity and their electronic nose data were collected.²⁸



Figure 7.10. Scentroid SC300. [Courtesy Scentroid, Canada]

Repeated impacts caused no skin rupture or leakage after treatment or during storage.²⁸ There was increasing dissimilarity among fresh blueberry fruits following mechanical injury, which supports the contention that greater quantitative and qualitative changes occur in blueberry volatiles.²⁸

Eight sample materials used in the car manufacture were studied for the discrimination of odors from trim plastic materials used in automobiles.²⁹ The tested samples included floor acoustic insulation, roof lining, rear trunk lining, heating pipe, window sealing, foam wire holder, and wiring.²⁹

Many different polymers were involved in the production of these materials, including polyurethane, EPDM, poly(ethylene terephthalate), polyolefin, PVC, and polypropylene.²⁹ It was possible to distinguish not only between different polymers but also between materials obtained from the same generic polymer.²⁹

Three electronic nose systems (Cyrano 320, FOX 3000, and QMB6) were used for odor analysis of solvents remaining in the printed food packaging.²³ All three systems were able to discriminate among film samples at various levels of retained solvents.²³ All three systems correctly identified 100% of unknown samples.²³ Based on discriminatory power and practical features, the FOX 3000 and the Cyrano 320 were superior.²³

Four rice samples of the long grain type were tested using an electronic nose (Cyrano-320).³⁰ The Cyrano-320 was able to differentiate between varieties of rice.³⁰ Further research is needed for developing analytical procedures that adapt the Cyrano-320 as a tool for testing rice quality.³⁰

Musty-aroma compounds such as geosmin impact the quality of fresh water and water-cultured raised fish and sea-food.³¹ *Streptomyces* bacteria are geosmin-producing microorganisms.³¹ Early detection of *Streptomyces* spores in reverse osmosis and tap water were investigated.³¹ Data indicates that an electronic nose can be employed to detect and monitor the early activity of *Streptomyces* in water at different stages of differentiation, as well as to discriminate between different species based on their volatile production patterns.³¹

Portable electronic noses were used for outdoor air monitoring of sewage odors directly in the field.³² Two commercial devices with different gas sensor technologies were tested: conducting polymer, CP, and metal oxide semiconductor, MOS, in order to select the most appropriate one for this application.³² The algorithm that permitted the least humidity, temperature and day correlation was selected.³² The results indicated that CP sensors appear to be unacceptable for this application while MOS sensors tested were better for discriminating between the different odors.³²

The above data shows that there is a considerable success in the application of electronic noses in various aspects of engineering. A variety of systems and 25-year long experience with electronic noses broadens the usefulness of their application.

7.5 ODOR DIGITIZATION

The function of odor digitalization is to control an output device (whiffer) to produce an imitation of an odor sensed by a distant input device (sniffer).¹⁹ The sniffer is designed to digitize the smell to preserve its informative features (the odor recipe) of the original odor input.¹⁹ In this manner, an e-nose can be used as the sniffer.¹⁹ Once the odor recipe of the target odor is determined, it can be transmitted through the network and then be reproduced anytime using the odor blender contained in the whiffer.¹⁹ The whiffer consists of a set of palette odors and the odor blender used to mix them in required proportions.¹⁹ The system is similar in action to the above described odor recorder.

7.6 SENSORY ANALYSIS (TEST PANEL EVALUATION)

Some standard methods are followed in the test panel evaluation. Flavor profile analysis method was developed in 1950 by Arthur D. Little Co. and it is still used with some amendments today.³⁷ The method is used for drinking water testing by test panel evaluation (some tasks included testing for the influence of pipe materials and other plumbing materials). The testing panel in this method includes 4-7 people who are trained for at least 2 days. Odor intensity is rated on a scale of 0 to 12 (0 taste-free) and 8 different odors and 4 tastes are recognized (chemical, medicinal, fishy, fragrant, swampy, grassy/woody, chlorinous, and earthy/musty; sour, sweet, salty, and bitter).³⁷

Many international standards exist regarding sensory analysis. The most important are given below:

ISO 3972:2011 Sensory analysis -- Methodology -- Method of investigating sensitivity of taste

ISO 5492:2008 Sensory analysis -- Vocabulary

ISO 5496:2006 Sensory analysis -- Methodology -- Initiation and training of assessors in the detection and recognition of odors

ISO 6658:2005 Sensory analysis -- Methodology -- General guidance

ISO 8586:2012 Sensory analysis -- General guidance for the selection, training and monitoring of assessors and expert sensory assessors

ISO 8589:2007 Sensory analysis -- General guidance for the design of test rooms

ISO 13300-1:2006 Sensory analysis -- General guidance for the staff of a sensory evaluation laboratory -- Part 1: Staff responsibilities

ISO 13300-2:2006 Sensory analysis -- General guidance for the staff of a sensory evaluation laboratory -- Part 2: Recruitment and training of panel leaders

ISO 13301:2002 Sensory analysis -- Methodology -- General guidance for measuring odour, flavour and taste detection thresholds by a three-alternative forced-choice (3-AFC) procedure

The above standards are selected from a total 35 ISO standards, which are related to the sensory testing. This shows extensive international effort in the development of these methods and importance of this testing method.

Also, many ASTM standards (58 active and 97 historical) exist on the subject. Some of the most essential are listed below:

ASTM D6165-97(2012) Standard Guide for the Comparison, Detection, and Identification of the Odors of Paints, Inks, and Related Materials

ASTM D7297-14 Standard Practice for Evaluating Residential Indoor Air Quality Concerns

ASTM E253-15b Standard Terminology Relating to Sensory Evaluation of Materials and Products

ASTM E460-12 Standard Practice for Determining Effect of Packaging on Food and Beverage Products During Storage

ASTM E544-10 Standard Practices for Referencing Suprathreshold Odor Intensity

ASTM E619-09 Standard Practice for Evaluating Foreign Odors in Paper Packaging

ASTM E679-04(2011) Standard Practice for Determination of Odor and Taste Thresholds By a Forced-Choice Ascending Concentration Series Method of Limits

ASTM D1292-15 Standard Test Method for Odor in Water

ASTM E1499-97(2009) Standard Guide for Selection, Evaluation, and Training of Observers

ASTM E1697-05(2012)e1 Standard Test Method for Unipolar Magnitude Estimation of Sensory Attributes

ASTM E1870-11 Standard Test Method for Odor and Taste Transfer from Polymeric Packaging Film

ASTM E1885-04(2011) Standard Test Method for Sensory Analysis—Triangle Test

ASTM E1909-13 Standard Guide for Time-Intensity Evaluation of Sensory Attributes

ASTM E2164-08 Standard Test Method for Directional Difference Test

ASTM E2454-05(2011) Standard Guide for Sensory Evaluation Methods to Determine the Sensory Shelf Life of Consumer Products

ASTM E2609-08(2016) Standard Test Method for Odor or Flavor Transfer or Both from Rigid Polymeric Packaging

ASTM E2610-08(2011) Standard Test Method for Sensory Analysis—Duo-Trio Test

ASTM D6399-10 Standard Guide for Selecting Instruments and Methods for Measuring Air Quality in Aircraft Cabins

Selection of ASTM methods shows that their emphasis is on specific, practical applications.

Below we discuss observations from published studies regarding testing methods used in these studies.

Virginia Tech is involved in research studies on the effect of plumbing materials on drinking water quality and odor.³⁸ In the studies of silane crosslinked PEX pipe contribution to chemical/solvent odors in drinking water, 10 panelists were recruited and trained for several weeks in a flavor profile analysis.³⁸ The procedure used followed the directions of standard procedure.³⁷ Samples for analysis had a temperature of 45°C.³⁷ Silane cross-linked PEX pipe contributed a “chemical/solvent” odor, perceived as “sweet” or “bitter”, with a strong burning sensation, to the drinking water both in the presence and absence of disinfectant.³⁸

The effect of pipe relining with an epoxy-lined copper pipe on odor formation in drinking water was the subject of studies.³⁹ Panelists repeatedly and consistently described a “plastic/adhesive/putty” odor in the water from the pipes.³⁹ The same method as described in the previous paragraph was used.³⁹

Effect of different cups on sour cream quality was evaluated.⁴⁰ The sensory panel consisted of 10 selected assessors (ISO 8586-1:1993) and the analyses took place in a pur-

pose-built sensory laboratory (ISO 8589:2007).⁴⁰ Prior to the analysis, the panel was trained in the definition and intensities of each of the attributes using sour cream with varying sensory properties (dark storage and exposed to light).⁴⁰ The sour cream cups were stored in darkness at 4°C for 5 days before they were exposed to light for 36 h in a specially designed light cabinet.⁴⁰ The temperature of the samples was 13 to 15°C.⁴⁰ The sensory attributes that were assessed included the total intensity of odor, acidic, sunlight, and rancid odor, the total intensity of flavor, acidic, bitter, sunlight, and rancid flavor.⁴⁰

Removal of odorous compounds emitted in gasses from rubber processing was done by ozonation.⁴¹ Panelists, 20–40 years old, participated in the olfactometry test.⁴¹ To prevent the interferences of ozone, the effluent gas passed a KI-packed column in which ozone was absorbed before entering the sampling bags.⁴¹ The gas samples were then moved to an odorless room for the panelists to conduct an olfactometry test.⁴¹ A scale of 1 to 10 was used, with 0 indicating no odor and 10 representing the maximum odor intensity.⁴¹ All the gas samples stored in 10 L Tedlar bags were tested within 24 hours without dilution.⁴¹

To evaluate the consequence of odor emissions by plastics and to determine the effect of odor reduction, the odor concentration measurement was recommended.⁴² The odor concentration of odorants is determined by presenting a panel with samples in decreasing dilutions with neutral gas, in order to determine the dilution factor at the 50% detection threshold (50% of panelists detect the gas sample as odorous).⁴² The odor concentration of the examined sample is the dilution factor at the detection threshold and is expressed as multiples of one Odour Unit per cubic meter, OU/m³, at standard conditions.⁴²

Odor and chemesthesis from brief exposures to plasticizer TXIB (2,2,4-trimethyl-1,3-pentanediol diisobutyrate) have been studied.⁴³ Each panelist participated in many hours of 12 testing sessions.⁴³ In a session, a panelist judged: odor, nasal chemesthesis, or ocular chemesthesis.⁴³ The vapor phase concentrations covered the range 7 ppt to 67 ppb.⁴³ In testing ocular chemesthesis, the panelist placed three vessels into the sleeve, as for testing of odor.⁴³ One tube at the top of a vessel connected to the eye-cup, with the other tube capped.⁴³ In nasal chemesthesis testing, the panelist placed two vessels into the sleeve, one with stimulus material and one without (blank).⁴³ The panelist placed the tube from one vessel to the left nostril and that from the other vessel to the right nostril. The panelist sniffed and sought to decide which side gave the stronger sensation.⁴³

Odor perception was tested as a new method of detection of early degradation of polymers.⁴⁴ Polyamide-66 was used as an example polymer.⁴⁴ The odor experiment was conducted with the aid of 15 participants (7 men and 8 women) between 20 and 30 years old.⁴⁴ The participants were required to be in good health and were screened for pregnancy, tobacco use, having colds, allergies and other sensitivities.⁴⁴ The participants were asked to sniff the headspace of the jars, put the cap back on and then estimate the odor intensity.⁴⁴ To avoid olfactory adaptation, a short break of 60 s was introduced after every 5th stimulus presentation.³⁸ The perceived odor intensity correlated with a deterioration in mechanical properties and the amount of degradation products released.⁴⁴

It should be noted that a work environment may cause olfactory loss, as was found in the case of injection molding workers processing acrylonitrile-butadiene-styrene copolymer.⁴⁵ Similar result was reported in the case of workers exposed to styrene in the rein-

forced plastics industry.⁴⁶ Smell and taste disorders may also be caused by many other reasons discussed elsewhere.⁴⁷

7.7 GC/MS

In GC/MS testing, sample preparation differs a lot. The following methods of sample preparation were used:

- absorption/desorption⁴⁸
- close loop stripping⁴⁹
- the fogging residue after dissolution⁵⁰
- leaching to water⁵¹
- solid phase microextraction³⁸
- thermal desorption/cold trap⁵²
- volatiles extraction from plastic material⁵³⁻⁵⁵

The above methods of sample preparation for GC/MS studies are discussed below.

Volatiles from refillable PET bottles were absorbed on Tenax TA (60–80 mesh) using a dynamic headspace sampling method.⁴⁸ A 200 g sample of the product was poured into 500 ml glass flasks, which were then sealed with plastic screw tops with a headspace adapter and placed in a water bath at 35°C.⁴⁸ The Tenax cartridge was then inserted into the glass flask, the headspace adapter was closed, and the sample gently stirred for 30 min in the sealed flask.⁴⁸ The volatile compounds were desorbed from the absorbent material by a Perkin Elmer ATD 400 automatic thermal desorption system.⁴⁸ The desorption temperature was 250°C and the desorption time was 5 min.⁴⁸

The closed-loop stripping analysis technique was used for extraction because of its selectivity in isolation of the volatile non-polar fraction of the organic compounds present in the water samples from PVC pipes.⁴⁹ The temperature of the water bath was 45°C, and the temperature of the carbon trap was 60°C.⁴³ Also, 50 g of sodium chloride was added to every 1-L sample of water in the salting-out process.⁴⁹

The fogging residue was obtained from polypropylene automotive parts on aluminum foil and 50% of which was dissolved in 10 mL of dichloromethane.⁵⁰ The solution was concentrated to about 2 mL by evaporating the solvent at room temperature and analyzed with GC–MS by injecting 1 µL.⁵⁰

Polyethylene pellets used for the production of HDPE pipes were about 4 mm in diameter and 2 mm thick.⁵¹ 32 g of pellets were placed into 250 mL odor-free water and shaken for four hours at 25°C.⁵¹ The water samples (10 mL of each) were tested using gas chromatography/mass spectrometry.⁵¹

Solid phase microextraction with 75 mm Carboxene-PDMS coated fibers was used to prepare a sample of odorants from PEX pipe.³⁸ The solid phase microextraction conditions were optimized by the addition of 6 g of NaCl to 30 mL of sample water.³⁸ The sample was stirred at 50°C for 20 min during which time the fibers were injected into the 10 mL sample headspace for sorption.³⁸

The sampling tubes were filled with Tenax GR, which is poly(p-2,6-diphenylphenylene oxide) with 23% graphitized carbon.⁵² The amount of the adsorbent in the glass tube was 225 mg.⁵² The filled tubes were thermally cleaned at 320°C for 8 h with a purified nitrogen flow.⁵² Volatiles from extrusion coating with LDPE were collected into the

Tenax tubes at two extrusion temperatures: 285 and 315°C.⁵² Known volume of air was drawn through the Tenax tubes using a calibrated air pump.⁵²

Volatiles from polyethylene packaging,⁵³ polypropylene irradiated with γ -rays,⁵⁴ and multilayer packaging,⁵⁵ which was γ -sterilized, were extracted by solvents. In the case of polyethylene packaging, the sample was steam-distilled at atmospheric pressure, and the distillate was methylenechloride-extracted.⁵³ Volatiles were extracted from the powdered polypropylene with dichloromethane for 1 h at room temperature.⁵⁴ The dichloromethane solution was dried over anhydrous sodium sulfate and concentrated to a total volume of 150 mL at 50°C by means of Vigreux distillation.⁵⁴ The irradiated packaging material was placed in a sealed vial and extracted three consecutive times with 2.5 mL of hexane (24 h, 40°C).⁵⁵ The solution was concentrated under a stream of pure N₂ to 200 μ L.⁵⁵

The purpose of the GC/MS testing is to identify and determine the concentration of volatiles in odorous materials. The test results of this method are discussed in many sections of this book, most frequently in chapters 3, 8, and 9.

7.8 GC/OLFACTOMETRY

GC/olfactometry uses human assessors as a sensitive and selective detector for detection of odor-active substances. Combination GC/MS studies with sensory analysis have two main purposes:

- identification of the most important odorant for a particular product
- assignment of odor quality to odorants.

Chapter 3 gives many examples of results of using this combination of methods. The most striking example was the identification of 8-nonenal as the main component of odors in polyethylene packaging⁵³ and assignment of odor qualities to 29 odorants in polypropylene and 38 odorants in the same polypropylene after its γ -irradiation.⁵⁴

The methods of GC/olfactometry panel training are discussed elsewhere.⁵⁶ Aroma extraction dilution method, detection frequency, and posterior intensity were used to evaluate abilities of trained panelists.⁵⁶

7.9 THRESHOLD ODOR NUMBER

The organoleptic properties of water were assessed according to EN 1622,⁵⁷ which is based on a quantitative dilution method.⁵⁸ Five dilutions of the test water samples were performed, and threshold odor number, TON, was assessed using a scale from 0 to more than 5.⁵⁸ Milli-Q water (TON=0) was used as a reference.⁵⁸ TON values higher than three were assigned to water samples with significant odor.⁵⁸

Threshold odor number was used in assessment of inertness of polyester-based bottle material.⁵⁹ Triangle test with forced choice evaluation was also used. A series of nine successive dilutions was prepared.⁵⁹ Each dilution was assessed by the sensory panel in a 3-AFC presentation.⁵⁹ The samples were allowed to equilibrate at 25°C for at least 2 h before being presented to the assessors.⁵⁹ An external panel of eight experienced assessors, two males, and six females, were paid to conduct the analyses.⁵⁹ The samples were evaluated in 2 h sessions per day for 8 days, i.e. 4 days each in two consecutive weeks.⁵⁹

The threshold odor number was also used for the assessment of odors from sewage treatment plant.⁶⁰

The highest dilution ratio that a panellist could detect, the odor strength (dimensionless number), is expressed with the unit of threshold odor number to characterize the organic precursors for chlorinous odor before and after ozonization.⁶¹ TON value (odor strength) is a geometric mean of TON values, obtained from four panellists.⁶¹ TON value was used in a round robin test for EN 1420-1 (Odor assessment for organic materials in contact with drinking water) with 14 contributing laboratories from 10 European countries segments using a plastic pipe for a migration test and an odour analysis of the migration waters.⁶²

7.10 SENSORS

In commercial and research electronic nose applications, the following sensors are used:^{21,63-69}

- conducting polymer, CP ((PMT, PPy, & PAN)²⁹ or PAN grafted to lignin)⁶⁸
- piezoelectric–surface acoustic wave, SAW
- piezoelectric–bulk acoustic wave (thickness shear mode, TSM)
- metal oxide semiconductor, MOS
- metal oxide semiconductor field effect transistor, MOSFET
- electrochemical, EC
- CTN-based sensors (single wall carbon nanotubes were modified with porphyrin units and applied as sensing materials in quartz microbalance sensors)⁶³
- very large chemical sensor (array consisting of 2^{16} (65,536) sensors)⁶⁴
- low threshold organic field effect transistors (contains an amorphous methoxy-derivative of poly(triaryl amine) as a semiconductor)⁶⁵
- polypeptide (has piezoelectric module chips)⁶⁶
- polymer-based microresistors⁶⁷
- molecularly imprinted polymers⁶⁹
- chemical sensor fabricated by inkjet-printing; carbon nanotubes-containing poly(ethylene naphthalate) was used for printing the sensing layers able to generate cross responses.⁷¹ Carboxylic acid functionalized single-walled carbon nanotubes were used in sensors embroidered into fabric substrates.⁷²

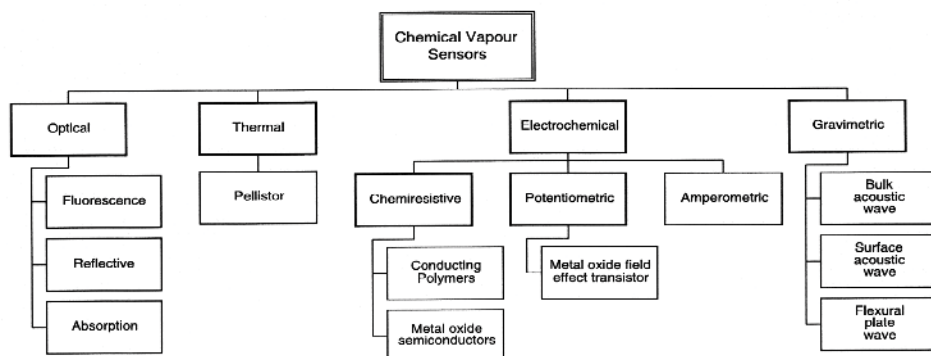


Figure 7.11. Principle of sensors utilized in electronic nose sensing. [Adapted, by permission, from James D, Scott S M, Ali Z, O'Hare W T, *Microchim. Acta*, **149**, 1-17, 2005.]

- the compounds having a polymeric structure based on Au-Au bonds whose generic formula was $[\text{Au}_2\text{Ag}_2(\text{C}_6\text{F}_5)_4\text{L}_2]_n$ were used to develop optical fiber sensors for identification of beverages by their odor.⁷⁴

Some of the above sensors and other sensors not listed above are given in the form of a diagram in Figure 7.11. Figure 7.11 also shows principles of action of sensors.⁷⁰ Below we discuss the action of sensors in more detail.⁷⁰

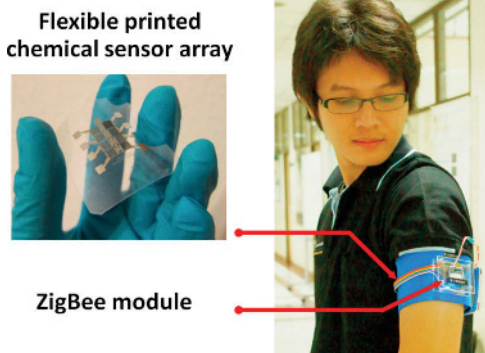


Figure 7.12. Wearable sensor. [Adapted, by permission, from Lorwongtragool, P; Sowade, E; Watthanawisuth, N; Baumann, R R; Kerdcharoen, T, *Sensors*, **14**, 19700-12, 2014.]

Figure 7.12 shows a wearable sensor obtained by inkjet printing.⁷¹ The sensor monitors volatiles released from skin during various activities.⁷¹

In conducting polymer sensors, polymer conductivity is altered in response to organic vapors.⁷⁰ Conducting polymers respond to a wide range of organic vapors with sensitivities of 0.1–100 ppm.⁷⁰ Their major drawbacks are the effect of humidity and sensor drift due to oxidation of the polymers.⁷⁰ Conventional, insulating, polymers can also be used by combining them with conductive fillers (metal powders, carbon black, or graphite) to create a composite.

Sorption of analyte gasses leads to swelling of the polymer, affecting the percolation network of the conductive particles in the composite, leading to a change in the direct current electrical resistance.⁷⁰

The two major types of piezoelectric sensors used in electronic nose sensing are a bulk acoustic wave and surface acoustic wave; flexural plate wave sensors have also been used.⁷⁰ The most common substrates for SAW are stress temperature compensated quartz or LiNbO_3 .⁷⁰ Two forms of SAW sensor exist, delay-line and resonator.⁷⁰ Piezoelectric crystals have a variety of organic coatings.⁷⁰

Metal oxide semiconductor sensors are one of the most commonly used electronic nose sensing technologies.⁷⁰ The outside of the sensor is coated with metal oxide, usually, SnO_2 doped with a small amount of Pd or Pt catalyst.⁷⁰ Many other oxides, including ZnO , WO_3 , and TiO_2 are also used.⁷⁰ There is a change in resistance on exposure to volatile compounds, which take part in redox reactions on the surface of the MOS, or to gasses such as NO , which act as oxidizing agents at MOS operating temperatures.⁷⁰ The change in resistance depends on the type of compound that reacts with the adsorbed oxygen on the sensing surface, as well as the metal oxide grain size.⁷⁰ Commercial sensors have typical sensitivities of 5–500 ppm.⁷⁰

Metal oxide semiconductor field effect transistor sensors have the structure of a metal insulator semiconductor and have sensitivity in the ppm region.⁷⁰ The common configuration transistor operates with three contacts: the source, the drain, and the gate.⁷⁰ Any reaction that causes a change in the metal gate or insulator properties results in a change in sensor's electrical properties and a change in the drain current.⁷⁰ The sensor

response is measured by the change in the gate voltage required to keep the drain current constant at a pre-selected value.⁷⁰

Electrochemical sensors measure current across a working and counter electrode as a function of analyte concentration in an electrochemical cell.⁷⁰ The working electrode is usually gold or platinum with a porous coating on the sensing side, allowing analyte gas to diffuse through to the electrode surface, which acts as a catalyst for electrochemical redox reactions.⁷⁰ They are sensitive to a small range of redox active compounds.⁷⁰

In carbon nanofiber-containing sensors, two strategies have been adopted to make sensor material.⁶³ One is the electropolymerization of pyrrole or pyrrole-substituted porphyrin monomers *via* formation of conjugated positively charged polypyrrole backbone, while negatively charged carbon nanotubes functionalized with carboxylic groups, which acted as a polymer dopant.⁶³ In the second case, the carbon nanotubes–porphyrin composites were chemically synthesized *via* the interaction between glycyl-substituted porphyrin and non-modified carbon nanotubes.⁶³ The application of carbon nanotube–porphyrin composite, both as the preconcentrator adsorbing phase and quartz microbalance coating, permitted a substantial sensitivity improvement as far as the possibility to measure volatile organic compounds, such as 1-butanol, in concentrations close to its odor threshold.⁶³

In the biological system, a large number of the olfactory receptor neurons are involved.⁶⁴ They are thought to enhance the sensitivity and selectivity of the system.⁶⁴ To explore this concept a polymeric chemical sensor array consisting of 2^{16} (65,536) sensors comprising tens of different types is being built.⁶⁴ A few tens of the conductive polymers showing broad and overlapped specificity to different volatile organic compounds are repeatedly deposited over the array elements.⁶⁴ Conductive polymers have been chosen as sensing materials because they have great sensitivity to a wide range of volatile compounds, wide selectivity, fast responses, as well as, low power consumption, and they operate at room temperature.⁶⁴

Organic semiconductors are now well established as cheap electronic materials in many applications.⁶⁵ The amorphous organic semiconductor, 4-methoxy-2-methyl polytriarylamine is used as an active layer for the organic field effect transistor.⁶⁵

Synthetic polypeptides have many advantages as sensing materials since they possess stable secondary structures due to cooperative H-bonding.⁶⁶ In an α -helical synthetic polypeptide, parallel and directional alignment of hydrogen bonds along the helical axis produces strong electric dipole moments and makes the peptide susceptible to electric and magnetic fields required for biosensors.⁶⁶ Site-specific functionalization is readily obtained.⁶⁶ They can be produced at a low price; high sensitivity and reversible response are well suited for long-term storage in dry, dissolved, and immobilized states.⁶⁶ Piezo-electric crystals used in this sensor were AT-cut spherical quartz crystals, with gold-plated metal electrodes.⁶⁶ The coating procedure was both gold electrode spin coating with 1.0 μ L polypeptide solution dissolved in DMSO, poly(n-butylmethacrylate) solution in xylene (1 wt%), or benzo-15-crown-5 in tetrahydrofuran solution (1 wt%).⁶⁶

The performance of a commercial electronic nose (Cyranose 320TM) for sensing indicator compounds (ethanol and acetic acid) associated with spoiled beef.⁷³

Pairs of polymer-coated quartz crystal microbalance sensors and polymer/carbon black-coated micro-resistance sensors have been used for the detection of headspace alcohol vapors.⁶⁷ Piezo-electric quartz crystal microbalances and micro-resistors sensors were

used.⁶⁷ The polymer coating on the micro-resistor sensor contained dispersed carbon black particles.⁶⁷ The ratio of the two responses is measured to obtain a characteristic value, which is directly related, *via* the mass and volume of odor, to its molecular density.⁶⁷

The poly(3-methylthiophene), PMT, and polyaniline, PAN, films were grown electrochemically onto glass substrates covered with ITO electrodes.²⁹ The polypyrrole, PPy, sensors could not be deposited onto ITO glass substrates due to the lack coverage between adjacent electrodes and were deposited onto alumina substrates covered with gold electrodes.²⁹ The PAN sensors were generated from solutions of aniline in deionised water, HBF₄, HCl, and HClO₄ as doping agents.²⁹ In all the cases, the concentration of dopant anions was 2 mol l⁻¹ and the sensors were deposited by potentiostatic technique.²⁹

Two approaches to molecular imprinting are known.⁶⁹ One is the preorganized approach, where the aggregates in solution prior to polymerization are maintained by (reversible) covalent bonds.⁶⁹ The other is the self-assembly approach, where the prearrangement between the print molecule and the functional monomers is formed by noncovalent or metal coordination interactions.⁶⁹ The second method avoids complicated synthesis and chemical cleavage steps.⁶⁹ The piezoelectric crystals were gold-deposited AT-cut. The polymerization reaction was induced by UV light radiation.⁶⁹ The sensor coated by imprinted polymers shows a frequency decrease of about 125 Hz.⁶⁹ A similar reduction in resonant frequency (~170 Hz) is obtained in the sensor coated by nonimprinted polymers.⁶⁹

Two methods can be used to fabricate the gas-sensing films for sensors:²⁴

- one-layer film-making method: the selected polymers were dissolved in methyl ethyl ketone solvent, and multiple-walled carbon nanotubes (1 wt%) were added.²⁴ The mixture was then magnetically stirred under ultrasonic oscillation to achieve uniform dispersion.²⁴ The uniformly mixed composite precursor was injected onto the chip using an HPLC syringe.²⁴ The solvent was removed, and the composite membrane formed by baking in a vacuum oven for 24 h²⁴
- two-layer film-making method: a multiple-walled carbon nanotube-modified electrode layer was prepared by drop-casting 1 mg/ml multiple-walled carbon nanotubes (1 wt%) dispersed in MEK onto the surface of an interdigitated micro-electrode device.²⁴ The MEK solvent was evaporated in air, at room temperature, to yield the multiple-walled carbon nanotube film.²⁴ The polymer films were deposited by drop-casting their solutions onto the multiple-walled carbon nanotube layer, followed by drying in vacuo, to form the multilayer films²⁴

Drift is an issue that affects the reliability of gas-sensing systems.⁷¹ Sensor aging, memory effects, and environmental disturbances produce shifts in sensor responses that make initial statistical models for gas or odor recognition useless after a relatively short period (typically a few weeks).⁷¹ Frequent recalibrations are needed to preserve system accuracy.⁷¹ An alternative approach is to use drift counteraction by signal processing techniques. Orthogonal Signal Correction, OSC, was proposed for drift compensation in chemical sensor arrays.⁷¹

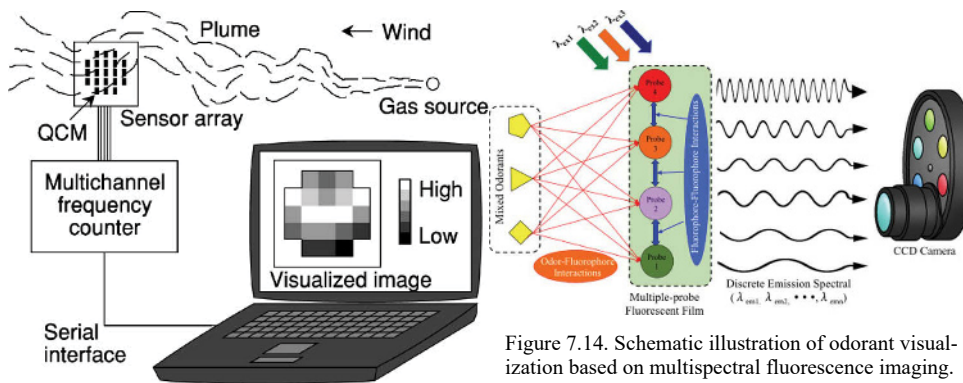


Figure 7.13. Schematic diagram of olfactory video camera. [Adapted, by permission, from Ishida H, Tokuhito T, Nakamoto T, Moriizumi T, *Sensors Actuators*, **B83**, 256-61, 2002.]

Figure 7.14. Schematic illustration of odorant visualization based on multispectral fluorescence imaging. [Adapted, by permission, from Yoshioka, H-T; Liu, C; Hayashi, K, *Sensors Actuators B: Chem.*, **220**, 1297-1304, 2015.]

7.11 VISUALIZATION

Changes in color of pH indicators (e.g., methyl orange, methyl red, thymol blue, phenol red, phenolphthaleine, and alizarin yellow) were observed when polyvinylpyrrolidone films containing these pH indicators were exposed to methanol and typical odor components of citrus fruits.⁷⁶ Color images were obtained from a scanner and they were color separated to red, green, and blue components. These three components were then converted into gray levels using integers from 0 to 255.⁷⁶

Charge transfer dyes, such as, 4-(dicyanomethylene)-2-methyl-6-(p-(dimethylamino)styryl)-4H-pyran and its derivatives have been developed for applications using them as photo- and electroluminescent materials for sensors.⁷⁷ A solvatochromism offers extended chemical selectivity for the differentiation of the organic solvents in a VOC-sensing performance.⁷⁷

The “olfactory video camera” is a sensing system that helps to locate the source of the gas odor.⁷⁸ It consists of a gas sensor array, multichannel frequency counter, and PC.⁷⁸ Figure 7.13 gives a schematic diagram of the system.⁷⁸

Figure 7.14 shows the application of multispectral fluorescence imaging to odorant discrimination and visualization.⁷⁹ The odorant induced a fluorescence change of the film under various excitation lights.⁷⁹ This was captured by a charge-coupled device camera to obtain multispectral images.⁷⁹ The use of multiple fluorescence probes provided discrete emission bands, which increased the dimensions of vector space of the multispectral images.⁷⁹

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ODOR IN RELATION TO DIFFERENT POLYMERS

8.1 ABS

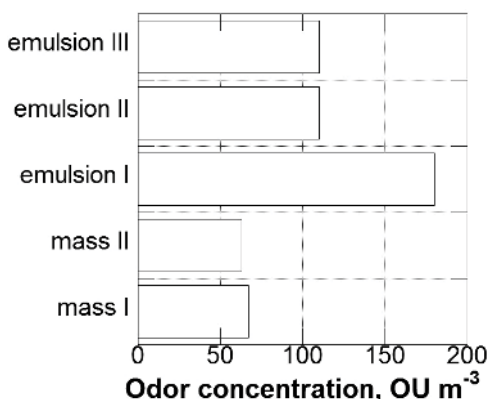


Figure 8.1 Odor concentration of different ABS-types determined by the method of olfactometry. [Data from Bledzki A K, Kessler A, Lieser J, *Polym. Testing*, **18**, 63-71, 1999.]

Figure 8.1 shows that there is a difference in odor produced by different ABS resins.¹ The reason for the higher odor concentration of the ABS types of emulsions is that these polymers contain emulsifying additives which lead to the increased emissions.¹

Early in the process of ABS production, it was found that mercaptan compounds such as lauryl mercaptan and tertiary octyl mercaptan are the most effective chain transfer agents.² However, mercaptan modified ABS polymers exhibit disagreeable odor characteristic of many sulfur-containing compounds.² It was found that incorporation of some metal salts helps in elimination of odor.² Salts

which are useful in this invention include barium chloride, barium stearate, cadmium chloride, cadmium stearate, cupric chloride, zinc chloride, and zinc stearate.²

Odor produced by ABS comes from processing at elevated temperatures.³ ABS resin contains acrylonitrile-styrene copolymer, SAN, in the matrix and grafted polybutadiene rubber in a dispersed phase.³ In products which require good heat resistance (e.g., electric/electronic appliances, outdoor advertisements, and automotive parts) some styrene is replaced by α -alkylstyrene.³ This resin is prepared by emulsion polymerization and low molecular weight, volatile products remain in the final product.³ This odor becomes an issue especially with car makers.³ In this invention, odor reduction was achieved by change of composition of ABS resin, which contains 25-45 wt% bulk polymerized, unsaturated nitrile-diene rubber-aromatic vinyl monomer resin, 5-15 wt% emulsion polymerized, unsaturated nitrile-diene rubber-aromatic vinyl monomer resin, 10-20 wt% bulk polymerized α -alkylstyrene-unsaturated nitrile-styrene resin, and 10-20 wt% solution polymerized N-substituted maleimide-unsaturated vinyl monomer resin.³

In another invention, a similar observation is conveyed that odor is formed by processing of any grade of ABS (emulsion, solution, bulk, suspension, or precipitation polymerization).⁴ This odor causes problems in ABS application in manufacturing parts used in car interiors.⁴ Elimination of odors in this invention is achieved by the addition of 0.5 wt% of either single or combination of zinc oxide and/or magnesium oxide, and 0.5–0.8 wt% of an epoxy compound, such as epoxidized soybean oil, epoxidized linseed oil, or alkyl epoxy stearate.⁴

Injection molding workers exposed to fumes of ABS had a lower olfactory function after work than the reference group (workers from another part of the factory).⁵ The decrease in olfactory function after 1 workday was statistically significant.⁵ The prevalence of abnormal olfactory function post-work in the exposed group was higher than in the reference group.⁵ The results of the pre-work comparisons indicate that the decreases in olfactory function recover after one night of rest.⁵ However, the cumulative effect of exposure to ABS over the longer term is uncertain.⁵ Many of the emitted compounds are potentially toxic, for example, styrene, toluene, ethylbenzene, acrolein, acrylonitrile, formaldehyde and other organic nitriles.⁵

It was found that a distinct rubber odor originates in a butadiene component contained in the ABS resin.⁶ This odor is prevented if ABS resin has a butadiene content in the range of 10 to 33 wt% based on the total component.⁶

8.2 ACRYLICS

Dispersions of copolymerizates of esters of acrylic acid and styrene possess intense, long-lasting odor that imparts their application in products used in closed rooms.⁷ In addition, acrylic esters are toxic.⁷ The odor is derived from unreacted monomers and oligomers.⁷ Several methods were used with limited success.⁷ The introduction of steam at normal or reduced pressure was highly foaming and caused coagulation.⁷ Distillation in thin-layer film evaporator was expensive and caused the formation of the undesirable crust and coagulation.⁷ Saponification of residual monomers removed acrylic ester odor but not that of styrene.⁷ New polymerization conditions helped to reduce residual monomer content to 3 wt%.⁷ This polymerization was combined with adjusting pH to 3–7 and addition of vinyl ester of alkanolic acid after polymerization at temperature 50–100°C.⁷ The residual monomer content was thus reduced to 0.35 wt% and the mixture was substantially free of odors.⁷

Halogen-containing acrylic rubber compositions are known to have an unpleasant odor and may cause skin irritation.⁸ Addition of α -olefins which have at least 4 carbon atoms, carboxylic acid vinyl esters, alkyl vinyl esters, lower alkyl cyclohexanes, and unsaturated dicarboxylic acid diesters solves the problem of odors and improves properties.⁸

Odor can be removed by addition of an odor-inhibiting agent selected from amine antioxidants and hindered phenols which reduce the odor of sterilized products.⁹

The following building products – floor varnish, latex foam backing, an acrylic sealant, and a waterborne wall paint – were studied.¹⁰ They emitted the following volatile compounds:¹⁰

- carpet: 2-ethyl-1-hexanol, 4-phenylcyclohexene, nonanal, and decanal
- sealant: hexane and dimethyloctanols

- floor varnish: butyl acetate, butoxyethanol, ethoxyethoxyethanol, 2-butoxyethoxyethanol, N-methylpyrrolidone
- wall paint: 2-butoxyethoxyethanol, decanal, 1,2-propanediol, Texanol

Depending on air velocity, the concentration of volatiles decreased over time.¹⁰ In order to reach an odor index of 0.1 (negligible), it took for carpet, wall paint, and sealant more than 7 weeks and for floor varnish, 3-5 weeks.¹⁰

Secondary emission products and reactive species from wood-based furniture coatings have been studied.¹¹ Relevant compounds included the wetting agent (2,4,7,9-tetramethyl-5-dicyne-4,7-diol), the plasticizer (di-2-ethyl-hexyl phthalate), aliphatic aldehydes, monoterpenes, photoinitiator fragments, acrylic monomers/reactive solvents.¹¹ Aliphatic aldehydes and some photoinitiator fragments have a strong odor, while acrylates and diisocyanates cause irritation of the skin, eyes, and upper airways.¹¹ Secondary emission products and reactive species can reach significant indoor concentrations.¹¹

Acrylic adhesive used in food packaging emitted the following odorous compounds: methyl methacrylate, butanol, butyl acrylate, 2-ethylhexyl acetate, acetic acid, 2-ethyl-1-hexanol, and camphor in larger concentrations.¹² The major odorous compounds were methyl methacrylate (56,200 ng g⁻¹), 2-ethylhexyl acetate (68,500 ng g⁻¹) and 2-ethyl-1-hexanol (514,000 ng g⁻¹).¹²

The smell of latex paint is caused by the trace amounts of volatile organic compounds that are not essential to the paint's function.¹³ The most abundant VOCs include acetone and n-butanol.¹³ They are present at concentrations between 1 and 2500 ppm, and do not affect performance properties, such as ease of application and hiding power.¹³ They are added to facilitate various steps in the paint's manufacture. Their removal eliminates the unpleasant smell.¹³

Methacrylic reactive resin cures with low odor.¹⁴ The reactive resins comprise high-boiling, reactive methacrylic monomers from the group of the polar, cyclically substituted esters of methacrylic acid.¹⁴

A decorative sheet includes a decorative base layer; an adhesive layer; and an odor absorbing scuff resistant layer.¹⁵ The odor absorbing scuff resistant layer includes an odor absorbing agent and silicone-acrylic particles.¹⁵ The decorative sheet maintains odor absorbing properties while being resistant to scuffs and scratches.¹⁵

8.3 ALKYD RESINS

Alkyd resins having high acid values can be made water reducible by neutralization of their free carboxyl groups with amine compounds such as triethylamine or diethanolamine.¹⁶ Compared with solvent-based alkyd resins, they have lower VOC, reduced odor, and lower flammability.¹⁶ Hybrid alkyd-acrylic dispersion is useful in VOC-free waterborne coatings with improved odor.¹⁷ Amine-neutralized, low odor, acrylic-modified paints form stable water dispersions with the very low solvent requirement.¹⁸

8.4 CELLULOSIC POLYMERS

Cellulose acetate is used as a fiber in tobacco filter.¹⁹ Chemical hydrolysis of cellulose acetate reduces its degree of substitution and produces free acetic acid.¹⁹ The presence of free acetic acid is undesirable in the filter because it causes the formation of a strong odor

and deteriorates the taste of tobacco.¹⁹ The invention solves this problem by controlling the progress of deterioration, which is also essential for use of cigarette filters, which, after being discarded in the environment, should be quickly biodeteriorated.¹⁹

Cellulose diacetate exposed to UVA radiation did not show any significant signs of deterioration, but, exposed to UVB and UVC radiations, it appeared discolored and released the typical vinegar odor.²²

Cellulose fibers are treated with an acidic odor-controlling agent.²⁰ Odor controlling agents include odor inhibitors and odor absorbers.²⁰ Partially neutralized hydroxyl multicarboxylic acids and polycarboxylic acids are used as odor controlling agents.²⁰ They serve as odor inhibitors to prevent or reduce the generation of ammonia and other basic odor-forming compounds, and also as odor absorbers of these compounds by neutralization and chelating reactions.²⁰ The main application of treated cellulose fibers is as absorbent cores of a variety of personal care and medical absorbent garments.²⁰

Cellulose fibers may also contain an odor-inhibiting agents, a biocide, an enzyme, or a urease inhibitor.²¹ Cellulosic fiber is impregnated with odor-inhibiting formulation to produce a fiber having odor inhibiting characteristics.²¹

8.5 CHITOSAN

α -Lipoic acid is an essential cofactor in mitochondrial multi-enzyme complexes related to energy production.²³ It is unstable under light or heat, and its decomposition is accompanied by an unpleasant odor.²³ Its stabilization by complex formation with the cationic polymer chitosan was investigated.²³ The α -lipoic acid-chitosan complex inhibited the decomposition of α -lipoic acid under heating.²³ The stability of α -lipoic acid in a product improved.²³ Chitosan is a promising biocompatible and biodegradable material for the stabilization of α -lipoic acid.²³ α -Lipoic acid is released from the complex by changing pH, which means that it is promptly released from the complex within a gastrointestinal tract after oral administration.²³

Chitosan film, incorporating green tea extract, was used as active packaging for shelf life extension of pork sausages.²⁴ The sensory qualities including odor, color, slime formation, and overall acceptability were improved when green tea extract was used.²⁴ Successful inhibition of lipid oxidation and microbial growth in the refrigerated pork sausages was possible with chitosan film incorporating green tea extract.²⁴ The results suggested that incorporation of green tea extract into chitosan film could enhance the antioxidant and antimicrobial properties of the film.²⁴

Chitosan/cellulose blend beads were prepared *via* homogeneous dissolution of chitosan and cellulose.²⁵ Deodorizing properties of these beads against trimethylamine were investigated.²⁵ Chitosan/cellulose beads which have a high specific area and high functionalities are useful for deodorants adsorbing noxious gasses.²⁵ The chitosan/cellulose blend beads have much better sorption activity than the cellulose beads as well as activated carbon.²⁵ The increased concentration of chitosan contributes to increased interaction between chitosan and trimethylamine and thus to increased sorption activity.²⁵

Odor reduction in disposable diapers, training pants, sanitary napkins, tampons, and medical dressing is obtained by addition of natural polymers.²⁶ Most odors from body fluids contain bacteria derived components and degradation products associated with biological functions.²⁶ Hydrogen sulfide, dimethylsulfide, dimethyltrisulfide, isovaleric acid,

ammonia, triethylamine, indole, and skatole are typical components of such odors.²⁶ Many additives were used to absorb or prevent the formation of these odorous substances, including activated carbon, zeolites, copper, metal oxides, alumina hydrate, holmite, laccinone, kaolin, and molecular sieves.²⁶ Acid/base interaction was also used to neutralize these odorous components.²⁶ An invention shows that triglycerides and polyglycosides enhance malodor absorption properties of chitosan and alginates.²⁶

Breathable absorbent articles contain chitosan to absorb odor.²⁷ These materials are useful in sanitary napkins, pantliners, nursing pads, and baby diapers.²⁷

An antimicrobial and odor-inhibiting article is made by vacuum deposition and electron beam techniques used to graft amino-reactive functional groups onto the polymeric material.²⁸ This is followed by contacting polymeric material with a chitosan solution.²⁸

8.6 CYANOACRYLATE

Compositions of methyl 2-cyanoacrylate have a pungent, unpleasant odor and produce an irritant effect on the nose and eyes.²⁹ Special ventilation procedures are necessary.²⁹ Methyl and ethyl 2-cyanoacrylates are much more volatile than 2-chloroethyl 2-cyanoacrylate, which has decreased odor.²⁹ An invention gives the method of preparation of 2-chloroethyl 2-cyanoacrylate, which has a boiling point of 134°C at 8 mm Hg.²⁹

An adhesive composition contains 2-cyanoacrylate and either a cyano-containing carboxylic acid epoxy adduct (e.g., cyanoacetic epoxy adduct) or a compound having a cyano group and carboxylic acid group in its molecule.³⁰ 2-Cyanoacrylate is volatile and, when cured by moisture alone, it cures for a long time and vaporizes, producing a strong odor.³⁰ The addition of the compounds of this invention makes the reaction rapid and eliminates production of odor.³⁰

The reaction rate of cyanoacrylates can be improved by the addition of an accelerator.³¹ Traditionally, amines are used for this application but they have a characteristic, strong odor. Some amines used had less odor but they were inconsistent in the efficiency of acceleration.³¹ The aromatic amine (e.g., N,N-dimethyl-p-toluidine/methyl- β -cyclodextrin or N,N-dimethylaniline/triacetyl- β -cyclodextrin) used in this invention helps to eliminate these problems.³¹

1,1-disubstituted ethylene monomers, such as α -cyanoacrylates can be used in the flavored monomeric adhesive which is useful as a medical adhesive.³² Flavoring compounds are added to these medical adhesives to control their smell.³² Some medical adhesives need to be sterile and the presence of flavoring compounds increases their viscosity due to polymerization, making adhesive not useful for its purpose of the application.³² Thymol and oil of wintergreen were found to be suitable flavoring agents, which can be used with medical adhesives which need sterilization.³²

Disadvantages of the known medical glues include insufficient storage stability and unpleasant odor (the odor bouquet is formed when cyanoacrylate and butylacrylate are mixed).³³ The medical glue, which comprises 3-methacryloxysulpholane, N-butyl-2-cyanoacrylate and a stabilizer has improved odor characteristics.³³

8.7 EPOXY RESIN

The epoxy lining is frequently used in drinking water pipe.³⁴ The formulation was based on bisphenol and amines with benzyl alcohol in hardener.³⁴ Threshold flavor number was high at 6 at one hour after application, and it was reduced to 2.5 after one day and stayed the same after one week.³⁴ Flavor detected was bitter almond.³⁴ The main products identified by GC/MS analysis included benzyl alcohol, monoglycidyl ether of butane diol, diglycidyl ether of butane diol, and diaminodiphenylmethane.³⁴ These volatiles were only present one hour after application.³⁴

Pipe relining *via in situ* epoxy lining was also used to remediate corroded plumbing or distribution systems.³⁵ Panelists repeatedly and consistently described a “plastic/adhesive/putty” odor in the water from the pipes with installed lining.³⁵ Significant odor occurred after 72 h of leaching, and short-term laboratory tests demonstrated that the odor imparted was proportional to stagnation time.³⁵ Water exposed to the epoxy liner for 72–96 h stagnation times also showed a significant increase in total organic carbon (0.4–0.6 mg/L) and a severe decrease in both free chlorine and monochloramine residual.³⁵

The acrylate-based photocurable systems with various radical-generating photoinitiators are currently used in most photocuring formulations because of their superior photo-reactivity as well as acceptable physical and mechanical properties.³⁶ The radical photocuring system has some drawbacks, such as strong odor and high irritation by monomers and oligomers.³⁶ As an alternative to photocuring technology, the cationic photocuring system offers a few useful advantages over the radical process including low odor.³⁶ Styrene oxide is a suitable diluent for cationic photocurable formulations to provide the requirements along with low viscosity and low odor.³⁶

The addition of compound having five-membered ring dithiocarbonate to epoxy resin composition inhibits emission of odors from the composition or cured article.³⁷

Low odor epoxy resin systems were obtained based on methyl nadic anhydride used as hardener and core-shell rubber.³⁸ The presence of the core-shell rubber reduced the strong odor that is normally produced in thermosets containing these anhydride hardeners.³⁸

A low-odor, low-viscosity hardener for epoxy resins is based on polyamine, which has at least one secondary amine group.³⁹ Hardener has only slight odor and it is fluid at room temperature so that it can be easily worked without additional thinners.³⁹

8.8 ETHYLENE-PROPYLENE DIENE TERPOLYMER, EPDM

The control of odors in the cabins of cars is one of the trends promising further expansion in the automotive industry. The odors in cars are due to the extensive use of polymeric materials inside the automobiles.⁴⁰ Floor acoustic insulation and window sealing elements were manufactured from EPDM and both contributed to the odor formation.⁴⁰

Objectionable odor from new and recovered EPDM rubber was found to come from ethylidene norbornene, which is a monomer used to produce sulfur curable ethylene-propylene rubbers.⁴¹ It has a very distinctive odor, which is present in minute quantities in the finished products.⁴¹ This odor can be reduced by addition of a crystalline silica molecular sieve in a sufficient amount.⁴¹

Peroxide systems are not often employed in EPDM because they require special vulcanization technique and cause the odor production.⁴²

A low odor, single element, cable connection cover is produced from EPDM.⁴³ This was achieved by the use of a low odor dilation composition which is a combination of non-aromatic compounds.⁴³ The dilation composition is a mixture of C7 to C8 aliphatic hydrocarbon (e.g., Soltrol 10) and fluorocarbon component (1,1-dichloro-1-fluoroethane).⁴³

Antimicrobial EPDM composition can be attacked by a number of microorganisms including *Escherichia coli*, *Staphylococcus aureus*, *Klebsiella pneumonia*, *Candida albicans*, *Pseudomonas aeruginosa*, and many others.⁴⁴ Antimicrobial formulation provides not only antibacterial benefits but also odor control properties.⁴⁴ Silver-based biocides were found useful in the EPDM compositions.⁴⁴

8.9 ETHYLENE-PROPYLENE RUBBER, EPR

Ethylene-propylene rubber can be vulcanized to thermoset materials with a crosslinking agent.⁴⁵ Many crosslinking agents cause the formation of bad odor.⁴⁵ Addition of 2.3 phr (0.0013 equivalents of active oxygen) of n-butyl- γ,γ -bis(t-butylperoxy) valerate gives an excellent odor rating.⁴⁵ Methyl- γ,γ -bis(t-butylperoxy) valerate and ethyl- γ,γ -bis(t-butylperoxy) valerate do not produce bad odor but are less efficient as crosslinkers.⁴⁵ γ,γ -Bis(t-butylperoxy) valeric acid and n-butyl- γ,γ -bis(t-amylperoxy) valerate produce odor.⁴⁵

Ethylene-propylene rubbers, which contain ethyldiene norbornene contain 1.3-butadiene, which has stringent control limit of air emission (1 ppm).⁴⁶ Ethyldiene norbornene has a strong odor, which can be detected in an ambient air at 13 ppb.⁴⁶

8.10 ETHYLENE-VINYL ACETATE, EVA

Ethylene-vinyl acetate copolymer does not have an acid odor if it is not thermally degraded.⁴⁷ But elevated temperature and presence of some additives (for example, high amounts of clay) cause the production of pungent, acetic acid odor, which is a product of thermal degradation of ethylene-vinyl acetate copolymer.⁴⁷

Use of dicumyl peroxide as a crosslinking agent gives ethylene-vinyl acetate foams strong, pungent odor of dicumyl peroxide.⁴⁸ Vegetable filler from coffee grounds eliminates this odor.⁴⁸

Fragrances and odor neutralizers can best be integrated with matrix polymer (in this invention with bioplastic, which has strong odor) by adding it with suitable polymeric material.⁴⁹ Ethylene-vinyl acetate copolymer beads can be impregnated with fragrances and/or odor neutralizers.⁴⁹ Ethylene-vinyl acetate copolymer has no odor of its own but can absorb or be permeated by fragrances.⁴⁹ For this reasons, ethylene-vinyl acetate copolymer is used as a host for fragrances in disposable air fresheners.⁵⁰ One or more fragrances can be used in this invention.⁵⁰

Polyvel Inc. has developed odor-managing masterbatches which are suitable for HDPE, LDPE, ethylene-vinyl acetate copolymer, polypropylene, and polyamide.⁵¹

Low odor coating composition for the paper was based on a vinyl acetate-ethylene copolymer emulsion.⁵² The low odor performance is partially attributed to factors, such as the structure/composition properties of the vinyl acetate-ethylene copolymer emulsion and

its advantages over commonly used styrene-butadiene copolymer emulsion.⁵² The vinyl acetate-ethylene copolymer emulsion is free of organic phenylic monomer and the polymerization process is carried out without addition of phenylic derived monomer, therefore, the residue of volatile phenylic derivative which has special odor such as 4-phenyl cyclohexene is avoided.⁵²

8.11 IONOMERS

Partial degradation of a certain type of cationic polyelectrolytes can lead to the generation of amine odors such as trimethylamine.⁵³

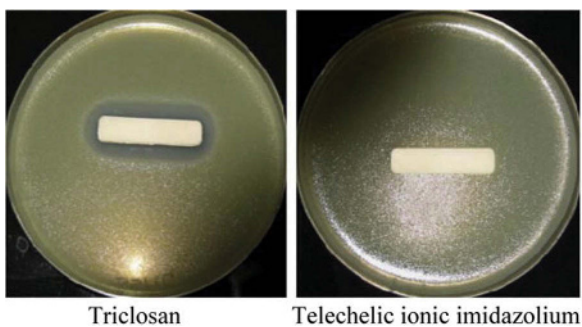


Figure 8.2. The agar plate assay of PBT with 2% Triclosan (left) and 2% telechelic ionic imidazolium (right). [Adapted, by permission, from Colonna, M; Berti, C; Binassi, E; Fiorini, M; Sullalti, S; Acquasanta, F; Vannini, M; Di Gioia, D; Aloisio, I, *Polymer*, **53**, 9, 1823-30, 2012.]

Sulfur odor from food can be removed by storing it in packaging material which contains a sulfur scavenger.⁵⁴ The sulfur scavengers were synthesized in an invention, namely, zeolite containing copper cations and molecular sieves.⁵⁴

Surlyn is an ionomer resin commercially available from DuPont. Its compounds have a mild methacrylic acid odor.⁵⁵

Poly(ethylene terephthalate) and poly(butylene terephthalate) are widely used as fibers for the textile industry and there is clear need for an antimicrobial treat-

ment that permanently inhibits the growth of microorganism that produce undesired odors.⁵⁶ Imidazolium poly(butylene terephthalate) ionomers can provide polyesters with a long-term antimicrobial activity.⁵⁶ The agar plate assay (Figure 8.2) shows significant difference in the mode of action between the 2% Triclosan (frequently used biocide) and polyester containing 2% of telechelic imidazolium ionomer.⁵⁶ Triclosan diffuses into the agar and gives rise to an inhibition zone around the sample whereas the imidazolium ionomers kill bacteria on contact with the surface.⁵⁶

The ionomer composition comprises an amine functional polymer compound reacted with silver halide, optionally together with a stabilizing component, such as an organic substance carrying a sulfonamide functional group.⁵⁷ The ionomer composition is suitable for use as an antimicrobial coating, antimicrobial finish, antimicrobial additive, and as antimicrobial component for formation of new antimicrobial materials.⁵⁷

8.12 NITRILE RUBBER

Nitrile rubber is produced by copolymerization of α,β -ethylenically unsaturated nitrile monomer, diene monomer and/or α -olefin monomer.⁵⁸ When the amount of the α,β -ethylenically unsaturated carboxylic acid is too large, an odor of the residual monomers in nitrile rubber may be strong.⁵⁸

Grinding wheels can be made with nitrile rubber.⁵⁹ When they are used for dry grinding smoke or fumes are emitted, which are described as acrid and nauseating.⁵⁹ The objectionable odor can be prevented if certain classes of diketones, which contain a conjugated system of two double bonds or unsaturated groups, are added.⁵⁹ Dibenzoylethylene, chloranil, and anthraquinone help to prevent odor formation.⁵⁹

An improved polymerization process using a molecular weight regulator makes it possible to produce nitrile rubbers having low emission values and giving vulcanizates which are useful in odor-sensitive applications.⁶⁰

8.13 POLYACRYLATE

Polyacrylate polymers are used as superabsorbents in consumer products.⁶¹ Disposable diapers and sanitary napkins are some of the products concerned.⁶¹ The problems surfaced when consumers complained about an off-odor in these products.⁶¹ Solid superabsorbent polymers were not odorous, but some became highly odorous when wet.⁶¹ This observation suggested the involvement of volatile hydrophobic compounds.⁶¹ Removal of vinyl ketones, and especially the 5-methylhex-1-en-3-one, from the monomers, used to prepare the polymers resulted in improved materials with little odor.⁶¹

Polyacrylate polymer is used as a thickener in hypochlorite solutions used as bleach compositions.⁶² Some bleach compositions have a strong unpleasant odor. It was found that by the regulating viscosity of solution with polyacrylate, the size of sprayed mist can be decreased and the yield value of liquid increased, which reduces odor.⁶²

The superabsorbent material for the absorbent core contains polyacrylate-based material.⁶³ The hydrogen in water is trapped by the polyacrylate due to the atomic bonds associated with the polarity forces between the atoms.⁶³ Polyacrylate provides an effective liquid fragrance or odor control composition which does not alter the properties of the adhesive.⁶³

8.14 POLYAMIDE-66

Polyamide-66 was selected as a model material and subjected to accelerated aging through thermooxidation.⁶⁴ After different degradation times, participants smelled at the headspace of jars with aged polymer and scaled their perceived odor intensity, and conventional analysis by GC/MS and tensile testing were performed to measure the volatile compounds released and accompanying changes in mechanical properties during degradation.⁶⁴ A 150% increase in perceived odor intensity occurred concurrently with a significant deterioration in mechanical properties, and an increase in the amounts of the degradation products released from the polymer matrix.⁶⁴ The degradation products identified by GC/MS included cyclopentanone, pentanoic acid, 2-methyl-pyridine, 2-ethyl-cyclopentanone, butanamide, pentanamide, 2-butyl-cyclopentanone, N,N-hexamethylene-bisformamide, 2-pentyl-cyclopentanone, caprolactam, azepane-2,7-dione, 2-cyclopentyl-cyclopentanone, 1-pentyl-2,5-pyrrolidinedione, and dibutyl phthalate.⁶⁴ For the same time period, very small changes in thermal and surface properties of PA-66 were observed. It can be concluded that odor determination can be applied as a very sensitive tool of early degradation of polymer.⁶⁴

8.15 POLYAMINE

Dimethyl sulfoxide is used in treatment of traumatic brain injury to prevent reduction in cerebral blood flow.⁶⁵ This treatment is hampered by a strong odor produced by the treatment.⁶⁵ An invention refers to a procedure which reduces odor related to treatment using polyamine to absorb dimethyl sulfoxide.⁶⁵

An odor eliminating cloth contains a porous inorganic substance, metallic oxide, and inorganic silicon compound carrying a polyamine compound.⁶⁶ This cloth eliminates odor of basic gases, acidic gases, neutral gases, and sulfur-containing compounds present in the air of a room.⁶⁶

Mixtures contain reaction products of one or more amines with one or more epoxides and additionally isocyanates.⁶⁷ Applying such mixtures to textile fabrics, especially polyester fiber fabrics, reduces or prevents unpleasant sweaty odor after physical exercise.⁶⁷ The effects are very durable to laundering.⁶⁷

Odor-absorbing fabrics are used for removal of dimethyl sulfoxide or associated odors.⁶⁸ Such odors may be likened to the smell of rotten eggs.⁶⁸ A modified polyamine is a biocompatible and a dermatologically compatible aqueous-soluble and/or oil-soluble polymer able to absorb odorous substances.⁶⁸

8.16 POLYANILINE

Polyaniline film has high capacity of generating a superoxide capable of degrading a variety of odor materials.⁶⁹ A polyaniline-containing film is attached to the base material which is used as a heat-conducting surface of a heat exchanger.⁶⁹ The heat exchanger can be used for a vehicle air conditioner having a degrading and deodorizing function or a sterilizing function of harmful microorganisms especially when combined with silver.⁶⁹ Polyaniline reduces oxygen into superoxide anion radical, which is active oxygen.⁶⁹ The obtained active oxygen degrades odor materials or substances such as microorganisms.⁶⁹

The polyaniline–curcumin–copper–cobalt hybrid composite is used as a fish freshness sensor.⁷⁰ It has ability to detect the total volatile basic nitrogen.⁷⁰ A low-cost gas sensors were developed to detect different artificial fruit aromas (apple, grape and strawberry).⁷¹ Polyaniline deposition by *in situ* polymerization technique on the inter-digitated area of the graphite electrode was accomplished using the line-patterning technique over tracing paper substrate.⁷¹

8.17 POLYBUTADIENE

In the syndiotactic 1,2-polymerization of 1,3-butadiene, offensive odor is produced from sulfur compound involved in polymerization.⁷² One method of reduction of odor is related to treating syndiotactic 1,2-polybutadiene with hydrogen peroxide, but this method has limited application because hydrogen peroxide may react with double bonds in polybutadiene.⁷² The method described in this invention includes polymerization of 1,3-butadiene to *cis*-1,4-polybutadiene.⁷² After polymerization, halogen acid or its salt is added. A special system of catalyst is discussed in the publication.⁷²

8.18 POLY(ϵ -CAPROLACTONE)

Poly(ϵ -caprolactone)/ β -cyclodextrin functional nanofibers were manufactured by electrospinning their mixture from chloroform/*N,N*-dimethylformamide (60:40).⁷⁴ The poly(ϵ -caprolactone)/ β -cyclodextrin nanocomposites, by virtue of having their β -cyclodextrin cavities free and unthreaded by poly(ϵ -caprolactone), could potentially be an ideal substrate for removing wound odors through the formation of inclusion compounds with odorants while providing an ideal environment for the wound to heal.⁷⁴

8.19 POLYCARBONATE

Polycarbonate compositions are redistributed by melt equilibration using diethyldimethyl ammonium hydroxide as a redistribution catalyst.⁷³ This catalyst produces odorless polycarbonate having a very low residual amine level.⁷³ Tetramethylene ammonium hydroxide was previously used.⁷³ Trimethylamine formed under extrusion conditions imparted unpleasant odor to polycarbonate. The change of redistribution catalyst results in elimination of odor.⁷³

The process of production of bisphenol A with reduced sulfur content and polycarbonate made from such a bisphenol A were developed.⁷⁶ A container comprising: a polycarbonate formed from a bisphenol A having a sulfur concentration of 0.5 to 15 ppm based upon the weight of the bisphenol A was produced.⁷⁶ During extrusion of polycarbonate, the heat could generate a transesterification in the presence of moisture that could result in an undesirable release of odor through the release of 3-mercaptopropionic acid or its degradation products.⁷⁶

8.20 POLYCHLOROPRENE

The presence of by-products in polychloroprene latex, for example, chloroprene dimers and other unidentified low molecular weight materials, can have an undesirable effect on its odor.⁷⁵ Even rigorously stripped latexes retain an undesirable odor.⁷⁵ In the past, masking odors by reodorants (vanillin, oil of wintergreen, terpineol, anisic aldehyde, oil of cloves, camphor, and coumarin) have been used.⁷⁵ Reduction of odor in polychloroprene can be accomplished by treatment of stabilized polychloroprene latex with a compound selected from ozone, hydrogen peroxide, alkali metal salts of halogen oxo acids, alkali metal salts of peroxy acids, and their mixtures.⁷⁵

A process for reducing odor in polychloroprene comprises treatment of a stabilized polychloroprene latex with a compound selected from the group consisting of ozone, hydrogen peroxide, alkali metal salts of halogen oxo acids, alkali metal salts of peroxy acids and their mixtures.⁷⁷

8.21 POLYETHYLENE

Polyethylene used for drinking water pipes should have very low odor and be very taste-neutral.⁷⁸ Typical criterion for very low odor is very low concentration of volatile carbon compounds in the material. A test known as the VW Audi test⁷⁹ determines volatile carbon fractions at 120°C. According to DIN^{80,81} and EN⁸² tests, odor is also assessed by a

panel of testers using a scale from 0 to 4. An electronic nose also is used for this purpose.⁷⁸

The odor in polyethylene is generally caused by oxidation of polymer or by catalyst residues, e.g., triethylaluminum used as cocatalyst in Ziegler catalysis.⁷⁸ Other possible causes are additives, such as Ca and Zn stearates, and their decomposition products.⁷⁸ These additives are used to bind HCl derived from Ziegler catalysts.⁷⁸ Because of these, it is frequently necessary to add odor-trapping additives to polyethylene or to carry additional steps, such as deodorization *via* aeration.⁷⁸

Low molecular weight components may also be part of the problem.⁷⁸ If polyethylene has too broad molecular weight distribution, it will comprise too many oligomers which could cause odor.⁷⁸ Narrow molecular weight can be obtained with Ziegler catalyst and metallocene catalysts but they require large amounts of free organic Al cocatalysts, which adversely affect odor.⁷⁸

Low odor composition described in an invention is a blend of high molecular weight ethylene copolymer and low molecular weight ethylene homopolymer or copolymer.⁷⁸ The low molecular weight polyethylene has only a small fraction of volatile carbon compounds (>70 mg/kg as determined by the Audi test).⁷⁹

In several research papers, components of odor were determined. The results are combined in Table 8.1.

Table 8.1. Volatile components in polyethylene.⁷⁶⁻⁸⁸

Type	Odor components
acids	acetic acid, propionic acid, propanoic acid, butanoic acid, 2,2-dimethylpropanoic acid, pentanoic acid, hexanoic acid, heptanoic acid, octanoic acid, nonanoic acid, decanoic acid, undecanoic acid, and dodecanoic acid
aldehydes	acetaldehyde, propanal, 2-propenal, 2-butenal, butanal, 2-methylpropanal, 2-pentenal, 2-methyl-2-propenal, 2-methylenebutanal, pentanal, 2-ethylacrolein, 2-ethylbutanal, hexanal, 4-methyl-3-pentanal, 4,4-dimethylhexanal, 2-hexenal, 2,3-dimethylpentanal, heptanal, octanal, nonanal, 8-nonenal, decanal, undecanal, tridecanal, tetradecanal, benzaldehyde, pentadecanal
aromatics	benzene, toluene, ethyl benzene, m- and p-xylene, o-xylene, styrene, isopropyl benzene, n-propyl benzene, ethyl methyl benzene, 1,3,5-trimethyl benzene, 1,2,4-trimethyl benzene, p-isopropyl toluene, naphthalene
esters	butyl acetate, butyl acrylate, ethyl hexanoate, hexyl acetate, propyl hexanoate, butyl hexanoate, ethyl octanoate, hexamethyl butanoate, isobornyl acetate, hexyl hexanoate, ethyl decadienoate, 2,2,4-trimethyl-1,3-pentanediole, isobutyrate

Table 8.1. Volatile components in polyethylene.⁷⁶⁻⁸⁸

Type	Odor components
ketones	3-methyl-3-buten-2-one, 3-methyl-2-butanone, 2-pentanone, 2,3-dimethylcyclobutanone, 3,3-dimethyl-2-butanone, 3-penten-2-one, 3-methyl-2-hexanone, 4,4-dimethyl-2-pentanone, 3-hexanone, 3-methyl-2-heptanone, 4-ethylcyclohexanone, 5-methyl-3-hexanone, 3-heptanone, 2-heptanone, butyrolactone, 7-octen-2-one, 6-methyl-5-hepten-2-one, methylisobutyl, methylheptadienone, dimethyl hexanone, dimethylheptanone, isopropylhexanone, propanone, 2-butanone, 2,4-pentadione, 2-pentanone, 3-methyl-3-pentene-2-one, 3-pentanone, 2-methyl-3-hexanone, 2-methylcyclohexanone, 3-methylcyclohexanone, 4-methylcyclohexanone, 3-methyl-3-heptanone, 4-heptanone, 2-octanone, 3-octanone, 2-nonanone, 5-nonanone, 3-decanone, 3-undecanone, 3-dodecanone, ethylcyclobutanone, ethylcyclohexanone
terpenes	δ -carene, α -farnesene, limonene, α -pinene, α -terpinolene
others	2,6-di-tert-butylbenzoquinone, 2,4-di-tert-butyl phenol, 4-methyl-2,6-ditert-butyl-phenol, pentamethylheptane

In fume samples,⁸³ heptanal, 3-hexanone, butanal, pentanal, octanal, nonanal, decanal, and undecanal were the source of the strongest odors. The increase in temperature of extrusion caused the formation of higher concentration of volatiles.⁸³

8-Nonenal was found to be an important contributor to the “plastic” odor in polyethylene packaging.⁸⁴ Its concentration increased with increased temperature of extrusion, increased addition of regrind and more coarse regrind, as well as with increased storage temperature.⁸⁴ Additives such as Irgafos 168 and Irganox 1010 reduced the amount of 8-nonenal.⁸⁴

The amounts and distribution of degradation products generated on extrusion of LDPE in a commercial extruder line depend on the extrusion temperature and the extruded film thickness.⁸⁶ High extrusion temperatures generate more compounds at higher concentrations in the smoke.⁸⁶ Thick films cool more slowly and allow the oxidation to proceed at high rates before the film is quenched, thus releasing degradation compounds in higher amounts than from thin films.⁸⁶ Catalysts and catalyst carrier systems, chain branching, and molecular weight distribution seem to influence the degradation pattern of polyethylene.⁸⁶ Recycled LDPE, compared with virgin LDPEs, releases less degradation products at lower smoke concentrations, presumably because reactive sites in the virgin polymer chains have reacted during the first extrusion and oligomers and catalyst carriers present in the virgin polymer should have evaporated.⁸⁶

A major migrating component from HDPE pipes was 2,4-di-tert-butyl-phenol, which is a known degradation product from antioxidants such as Irgafos 168.⁸⁷ The test water from five out of seven brands of HDPE pipes showed threshold odor number, TON, higher than 4, and thus significant odor.⁸⁷ The total amounts of VOC were proportional to TON in the test water from most of the HDPE pipes.⁸⁷

There were substantial differences between different granulates used for the production of drinking water pipes.⁸⁸ Typical odor and taste types detected were, as follows: sweet, chemical, stale, dirty, metallic, stony, dusty, and plastic.⁸⁸ It was possible to associate odor components with odor types.⁸⁸

Ionizing radiation sterilization of HDPE caused change in odor and taste at doses close to the typical doses of sterilization (30-60 kGy).⁸⁹ At lower doses no change was observed.⁸⁹ Much earlier changes were observed in irradiated LDPE packaging material.⁹⁰ Plastic odor, burnt, pungent was observed already after exposure to 7.2 kGy, and the odor increased with the dose.⁹⁰

The odor intensity generated by the HDPE pipe remained relatively constant for multiple water flushes, and the odor descriptors were affected by disinfectant type.⁹¹ Water exposed to HDPE pipe demonstrated a significantly lower disinfectant residual than did the glass control.⁹¹

Primary LDPE scrap may be used in the composite film without any compromise in migrational, barrier, mechanical, and organoleptic properties.⁹²

Carbonyls are the major odor drivers in the overall odor formation in polyolefins.⁹³ Carbonyls are formed at moderate temperatures well below the typical processing temperatures.⁹³ The conventional antioxidants can prevent or reduce their formation.⁹³

8.22 POLYETHYLENE, CROSSLINKED

New silane-crosslinked polyethylene, PEX, pipe exposed to chlorine, monochloramine or no disinfectant produced odors in the leachate which were described as “chlorinous” if chlorine or monochloramine were present and “chemical/solvent-like” with descriptors of sweet, bitter, chemical, solvent, plastic, burnt and mechanical/motor oil.⁹⁴ The presence of disinfectant (chlorine or chloramine) did not alter the odor characteristics or intensity of the PEX odor.⁹⁴ The odors persisted after multiple flushing.⁹⁴ 2-Ethoxy-2-methylpropane, ETBE, was identified as a contributor to the odor from the PEX pipe.⁹⁴ Concentrations of ETBE in pipe leachate ranged from a low of 23 mg/L to >100 mg/L.⁹⁴ The concentrations decreased with increased flushing.⁹⁴ Panelists were able to smell ETBE at a concentration of 5 mg/L.⁹⁴ Several methods of processing exist.⁹⁴ Not all PEX materials display identical characteristics under similar conditions.⁹⁴

In another study, the predominating VOC in the test water from PEX pipes was methyl-tert-butyl ether, MTBE, (degradation product of Irgafos 168).⁸⁷ Several identified (tert-butanol, 4-butoxy phenol, 5-methyl-2-hexanone, ionol, mesityl oxide, tert-butyl isobutyl ester) and unidentified compounds were encountered in the test water samples.⁸⁷ Some of these components appeared in the test waters from two tested PEX brands, whereas others were specific to individual brands.⁸⁷

Eleven regulated and unregulated contaminants were found in a PEX plumbing system.⁹⁵ The odor and TOC levels decreased for six PEX brands sold in the USA during 30 days trial.⁹⁵ PEX pipes produced an odor that exceeded the USEPA SMCL even on the 30th day of trial.⁹⁵ Disinfectant exposure sometimes caused greater odor levels in PEX pipes.⁹⁵ Nine specific compounds identified to migrate from polyethylene and crosslinked polyethylene to drinking water were investigated.⁹⁶ Eight out of the nine compounds studied reach consumers with only minor concentration decrease during water distribution.⁹⁶

8.23 POLY(ETHYLENE TEREPHTHALATE)

Poly(ethylene terephthalate), PET, is one of the most common packaging materials. There are no published articles which may indicate that polyester directly contributes to odors of products. It is known for its excellent barrier properties against odors.⁹⁷ There may be circumstances in which PET regrind is contaminated because of previously stored products⁹⁸ or odorous products are formed during sterilization.^{90,99} Its composition is frequently important since it may need to provide a UV barrier to protect the product inside the package.¹⁰⁰ These subjects are discussed below in sequence.

Odors from waste or foodstuffs are frequently retained by containers or films having odor barrier properties.⁹⁷ Such odors are typically caused by hydrogen sulfide, methyl mercaptan, ethyl sulfide, dimethyl disulfide or diethyl disulfide.⁹⁷ Films having odor barrier properties are used as ostomy bags, trans-dermal delivery systems, cosmetic patches, incontinence bags, medical collection bags, and parenteral solution bags, as well as food packaging and protective clothing and in soil fumigation applications.⁹⁷

Mineral water and soft drinks with a perceptible off-odor were analyzed to identify contaminants originating from the previous misuse of the refillable poly(ethylene terephthalate) bottle.⁹⁸ Substances responsible for the organoleptic change were 2-methoxynaphthalene, dimethyl disulfide, anethole, petroleum products, ethanol with isoamyl alcohol, and ethers.⁹⁸ The moldy/musty odor was caused by trichloroanisole.⁹⁸ The off-odors originated from previous consumer misuse of food products (liquorice-flavored alcohol, home-made alcohol containing fusel oil) or non-food products (cleaning products, petroleum products, oral moist snuff and others).⁹⁸ No consumer misuse (e.g., deterioration of the original product and possibly storage in an unsuitable location) also contributed to the formation of off-odors.⁹⁸

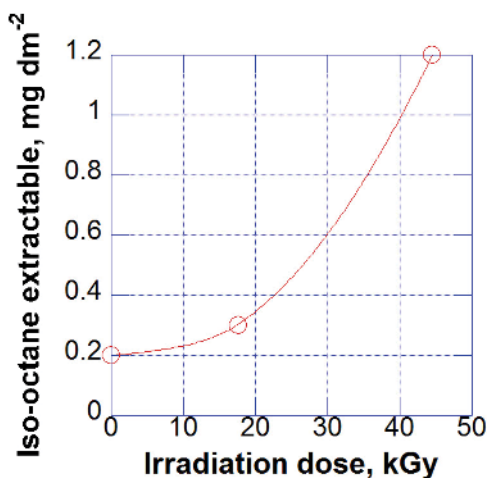


Figure 8.3. Amount of extractable substances from irradiated (⁶⁰Co) packaging materials obtained with iso-octane (24 h, 40°C, total immersion). [Data from Welle F, Mauer A, Franz R, *Radiat. Phys. Chem.*, **63**, 841-44, 2002.]

Irradiation of packaging materials leads to a formation of free radicals and ions, with secondary effects such as cross-linking as well as oxidative chain scission.⁹⁰ These reactions produce volatile radiolysis products.⁹⁰ The concentration of additive-related degradation products, e.g., 1,3-di-tert-butylbenzene or 2,4-di-tert-butylphenol increases during irradiation.⁹⁰ Figure 8.3 shows the effect of irradiation dose on the amount of extractable substances.⁹⁰ In this research, PET was compared with LDPE, PP, and PA and it was the most resistant polymer to irradiation.⁹⁰

Tensile testing, overall migration tests, and sensory tests were used to evaluate the effects of γ -irradiation (5–60 kGy) on six commercial semirigid packaging materials.⁹⁹ PET was the most radiation-resistant material.⁹⁹ Only a slight odor was observed after 60 kGy.⁹⁹

Chemical, microbiological, and sensory changes in milk stored at 4°C under fluorescent light were studied for a period of 13 days.¹⁰⁰ Milk container 1 l bottles made of clear PET + UV blocker with a transparent label, clear PET + UV blocker with a white colored label, clear PET, and PE coated paperboard carton.¹⁰⁰ Based on sensory evaluation the shelf life of milk packaged in clear PET is 8–9 days.¹⁰⁰ The shelf life of milk in clear PET containing a UV blocker and paperboard cartons is approximately 10–11 days.¹⁰⁰

Odor episodes were detected in drinking water in South America which was traced to pollution from a polyester production plant.¹⁰¹ The water samples contained high levels of 2,4-di-tert-butylphenol.¹⁰¹ When submitted to olfactory-GC/MS, the extract revealed the presence of an intense sweet-fruity odor.¹⁰¹

The layered double hydroxide intercalated with salicylate and carbonate anions dispersed in a solvent-based heat seal were coated on the surface of commercial poly(ethylene terephthalate) in an antimicrobial packaging system.¹⁰² The shelf life of the packaged Mozzarella cheese was increased by 20 days.¹⁰² The coating exerts an inhibitory effect on the microorganisms responsible for spoilage phenomena, without affecting the functional microbiota of the product.¹⁰²

Catalytic removal of odors and hazardous gasses at room temperature without using energy for heating was made possible by the developed technology of filter having Au/ZrO₂ catalyst on the poly(ethylene terephthalate) nonwoven fabric support.¹⁰³ Zirconium oxide particles were deposited on PET nonwoven fabric in the presence of 3-methacryloxypropyltrimethoxysilane to form a thin layer.¹⁰³ Then gold nanoparticles were deposited on ZrO₂ fine particles by deposition-precipitation method.¹⁰³

8.24 POLYISOPRENE

The liquid polyisoprene rubber prepared by thermal decomposition has a very strong odor.¹⁰⁴ Liquid polyisoprene rubbers, which are prepared by anionic polymerization using lithium catalyst, do not have odor.¹⁰⁴ Low molecular weight cis-polyisoprene liquid had some odor.¹⁰⁵

8.25 POLYIMIDE

The poly(amic acid) used as a precursor of polyimide is often decomposed into an amine terminal radical and an acid anhydride terminal radical by depolymerization due to reaction equilibrium when it is stored in its liquid state when it is processed into a desired shape, or when subjected to thermal imidification.¹⁰⁶ The characteristics and quality of polyimide are deteriorating and an offensive odor is produced due to diamine compound produced as a result of decomposition.¹⁰⁶

Imides reduces odors, especially of amine and ammonia.¹⁰⁷ Partial hydrolysis of polyimide provides water soluble polyimide that is suitable for odor removal.¹⁰⁷ Synergistic mixtures of zeolite and polyimide provide superior relief from objectionable odors.¹⁰⁸ It removes odor from animals, carpets, clothes, hands or other body parts.¹⁰⁸ Preferred zeolites include clinoptilolite, chabazite, mordenite, and silicalite.¹⁰⁸ The polyimide is present in the mixture in an amount up to 50 wt% (preferably 0.1 to 5 wt%).¹⁰⁸ The odor removing composition is in a form of powder.¹⁰⁸

A flexible NO₂ sensor was developed based on a tungsten trioxide nanoparticle-loaded, multiwalled carbon nanotube, reduced graphene oxide hybrid on a polyimide/poly(ethylene terephthalate) substrate.¹⁰⁹

The organic amine compound was dissolved in a solvent and converted into an amine salt of the specific polyimide precursor.¹¹⁰ The odor unique to the amine compound was suppressed.¹¹⁰

8.26 POLYOXYMETHYLENE

Polyoxymethylene produces formaldehyde, which is a source of odor.¹¹¹ In most applications, the odor cannot be detected but in some applications, such as closed containers, minute amounts of formaldehyde may be objectionable.¹¹¹ The least detectable concentration of formaldehyde is 0.8 ppm, and the irritating odor is detected at 5 ppm.¹¹¹ An invention suggests the addition of aminosulfones to eliminate this odor.¹¹¹ Another method of synthesis also indicates the presence of formaldehyde odor.¹¹²

In shaped articles, under standard conditions of temperature and pressure, formaldehyde slowly diffuses out of the article and may create a substantial odor nuisance.¹¹³ An invention proposes the use of inert gas at elevated temperature (80°C and above), which flows around shaped objects until formaldehyde is detected.¹¹³ If the sufficiently low temperature is employed, no structural changes are observed.¹¹³

Another patent describes the method of production of low odor polyoxymethylene, which has odor-reducing additive selected from a group consisting of low molecular weight primary or a secondary amine of low volatility, succinimide, anthranilic acid, and aminobenzoic acid.¹¹⁴ The mixture shows a synergistic effect in reducing formaldehyde odor.¹¹⁴

The polyoxymethylene is end-capped with a siloxane linkage that can prevent degradation of the polymer and subsequent emission of VOC degradation products such as formaldehyde.¹¹⁵ Formaldehyde as well as other VOC emissions lead to an unpleasant odor and can raise environmental health concerns.¹¹⁵

8.27 POLY(PHENYLENE ETHER)

Odor-producing components, such as 2,4,6-trimethylanisole and 7-methyldihydrobenzofuran, are removed from poly(phenylene ether) by continuous distillation and recycling of aromatic solvent.¹¹⁶ It is known that 10 ppm of 2,4,6-trimethylanisole can be detected by consumers.¹¹⁶ The odor is especially strong when the material is heated in a microwave oven.¹¹⁶

In another invention, 2,4,6-trimethylanisole, 7-methyldihydrobenzofuran, dihydrobenzofuran, 2,6-dimethylcyclohexanone, ethylhex-2-enal, dibutylamines, and various unsaturated amines are removed by extraction with acetone.¹¹⁷ All these odor components are by-products of synthesis, with the exception of amines, which are produced during extrusion of poly(phenylene ether).¹¹⁷ Vacuum venting is not sufficient to remove all odorous substances. Extraction with acetone is able to remove over 99% of odorous substances.¹¹⁷

In a further development, the low odor poly(phenylene ether) is made from a polymerization grade phenolic monomer, which has been crystallized from a solvent.¹¹⁸ The

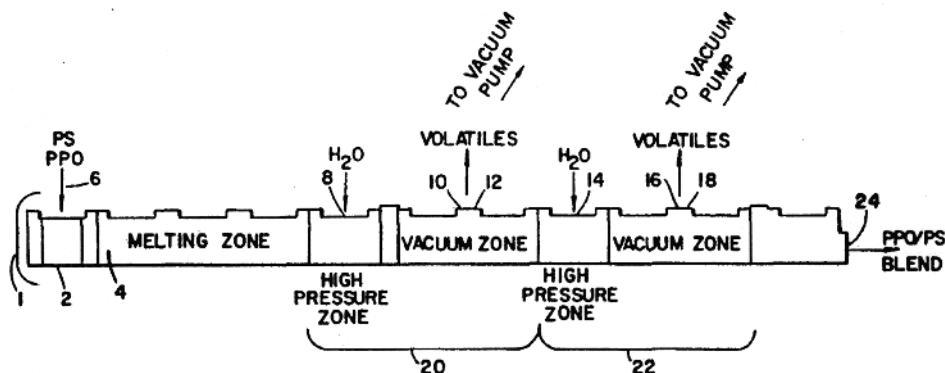


Figure 8.4. Schematic diagram of extruder for devolatilization of poly(phenylene ether). [Adapted from Benevicius J P, Hasson A, Pecak W E, US Patent 5,204,410, General Electric Company, Apr. 20, 1993.]

odor-causing impurities which are removed by crystallization include 2,4,6-trimethylanisole and 7-methyldihydrobenzofuran.¹¹⁸ An amine-free catalyst (manganese catalyst) is used.¹¹⁸

Low odor poly(phenylene ether) can be produced by mixing it with water and distillation of odorous substances with steam from the boiling water.¹¹⁹

Volatile substances in poly(phenylene ether) are substantially reduced by extruding the resin using plurality stages comprising water injection and vacuum venting.¹²⁰ Figure 8.4 shows the schematic diagram of the extruder used for this purpose.¹²⁰

A method of purification a poly(phenylene ether) to reduce odors includes mixing a poly(phenylene ether) solution with first washing solvents including a C1-C4 alkanol and water and a second liquid phase comprising C1-C4 alkanol and water, and separating the first liquid phase from the second liquid phase.¹²¹

8.28 POLYPROPYLENE

Table 8.2 gives information on the odor-active compounds, which were found in extracts from neat polypropylene.¹²²

Table 8.2. The odor-active compounds found in extracts from neat polypropylene. [Data from Tyapkova O, Czerny M, Buettner A, *Polym. Deg. Stab.*, **94**, 757-69, 2009.]

Odorant(s)	Odor type
hexanal	grassy
octanal, nonanal	soapy
oct-1-en-3-one, non-1-en-3-one	mushroom
(Z)-non-4-enal, (Z)-non-2-enal	fatty
acetic acid	vinegar
(E)-non-2-enal	cardboard
(E,Z)-nona-2,6-dienal	cucumber
(Z)-dec-2-enal	plastic

Table 8.2. The odor-active compounds found in extracts from neat polypropylene.
[Data from Tyapkova O, Czerny M, Buettner A, *Polym. Deg. Stab.*, **94**, 757-69, 2009.]

Odorant(s)	Odor type
butanoic acid	cheesy
2-/3-methylbutanoic acid	fruity
hexanoic acid	musty
(tr)-4,5-epoxy-(E)-dec-e-enal	metallic
γ -nonalactone	coconut
4-methylphenol	horse
γ -decalactone, γ -udecalactone, γ -dodecalactone	peach
3-ethylphenol	leather
ethyl vanillin, vanillin	vanilla
phenylacetic acid	bee wax

Many different methods of odor removal were invented. In isotactic polypropylene, the odor-producing compound was unsubstituted and substituted benzoic acid.¹²³ Ethyl benzoate and ethyl anisate are used in conjunction with titanium catalyst.¹²³ Isotactic polypropylene containing odorant was mixed in a molten state with a transesterification compound.¹²³ The following transesterification compounds are suitable: partially esterified glycerol, epoxide, monofunctional and polyfunctional alcohols, aliphatic acid ester, and their mixtures.¹²³

Rosin esters were used to reduce the tendency of shaped articles from polypropylene to form odorous decomposition products upon γ -irradiation.¹²⁴ The odor-producing compounds include formic, acetic, or butyric acids generated by scission of polymer chains.¹²⁴ Rosin ester is added in a concentration of 0.095 to 1 wt% together with normal stabilizers used in polypropylene.¹²⁴

Deodorization of odorous polyolefins is accomplished by mixing them with low concentration levels of an inorganic oxidant (ammonium perchlorate, potassium perchlorate, sodium perchlorate, sodium chlorate, potassium chlorate, sodium peroxide, sodium perborate, hydrogen peroxide, and their mixtures).¹²⁵ Optionally, fragrance (lemon oil, lime oil, mandarin oil, verbenal, lemon-grass oil, or their mixtures) can also be added.¹²⁵

The addition of 10 wt% CaCO_3 to polypropylene substantially reduces its odor.¹²⁶ The product becomes microwaveable.¹²⁶ Acidic fillers, such as mica, natural clay minerals (kaolinite, bentonite, attapulgite, montmorillonite, clarite, and Fuller's earth), are particularly detrimental in generating odor compounds when processed under high shear and high temperature in a twin screw extruder.¹²⁶

Polypropylene having agreeable odor characteristics is produced with the addition of di-*t*-amyl peroxide and at least one of its decomposition products.¹²⁷ Additives that can negatively impact odor and taste (e.g., thioesters) are generally avoided in resin formulation for food applications.¹²⁷ Also, use of 2,5-dimethyl-2,5-di-*t*-butylperoxyhexane should be discouraged because it yields butyl alcohol which is a highly odorous substance.¹²⁷

Emissions from polypropylene may cause the undesired smell, be harmful, or lead to fogging which prohibits its use for car interiors.¹²⁸ Typically alkanes, alkenes, and dialk-

enes dominate GC/MS chromatograms of polypropylene.¹²⁸ Emission depends rather on sample surface than on sample mass.¹²⁸ Substantial differences are between different grades of polypropylene.¹²⁸

γ -Irradiation causes both degradation of odorous substances and their formation. Table 8.3 shows which odor components are degraded and which are produced.

Table 8.3. The compounds generated during γ -irradiation and those which were degraded during γ -irradiation. [Data from Tyapkova O, Czerny M, Buettner A, *Polym. Deg. Stab.*, **94**, 757-69, 2009.]

	Odorants
generated by γ -irradiation	pentanoic acid, 4-methylhexanoic acid, hexanoic acid, 2,3-butanedione, (Z)-hex-3-enal, γ -dodecalactone, 2-Methylpropanoic acid, 2,3-pentanedione, acetic acid, γ -decalactone, phenylacetic acid, hex-1-en-3-one, 2-methylhexanoic acid, butanoic acid, 4-methylpentanoic acid, γ -undecalactone, 2-/3-methylbutanoic acid, 3-ethylphenol, 3-propylphenol, octanoic acid
degraded by γ -irradiation	Nonanal, (E,Z)-nona-2,6-dienal, non-1-en-3-one, hexanal, γ -nonalactone, (Z)-non-4-enal, (Z)-dec-2-enal, ethyl vanillin, octanal, (E)-non-2-enal, oct-1-en-3-one, (Z)-non-2-enal

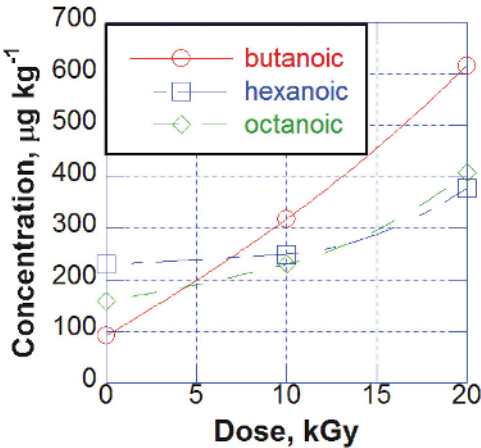


Figure 8.5. Effect of dose on generation of different acids in polypropylene exposed to γ -radiation. [Data from Tyapkova O, Czerny M, Buettner A, *Polym. Deg. Stab.*, **94**, 757-69, 2009.]

Figure 8.5 shows that the amount of odorant increases with a dose of radiation received by the material.¹²²

It was confirmed that food irradiation approved doses of 5 and 10 kGy do not cause significant changes in migration of odorous components, but sterilization doses (30 and 60 kGy) do.⁹⁹ Also, the amount of isooctane extracted substances increases with radiation dose increasing.⁹⁰

Shredded cabbage samples were packaged in three forms of packaging: bags of monooriented polypropylene film, polyethylene trays overwrapped with a multilayer polyolefin, and in a plasticized PVC film.¹²⁹ Polypropylene samples were significantly better in their general appearance but developed an off-odor.¹²⁹

During storage, 0%-fat yogurt conditioned in glass displayed the lowest aroma quantity decrease of the three types of packaging (glass, polypropylene, polystyrene), in accordance with the olfactory properties.¹³⁰ Polystyrene packaging seemed to be preferable for limiting aroma compound losses and subsequent fruity note intensities, and for avoiding the development of odor and aroma defects.¹³⁰ Less significant packaging effect was observed for 4%-fat yogurts.¹³⁰

Ethyl octanoate and linalool were scalped from wine into plastic films.¹³¹ Ethyl octanoate was sorbed more into polypropylene than into LLDPE, and at much higher extent

than linalool, as a consequence of the different polarities of the molecules.¹³¹ The amount of ethyloctanoate lost at the steady state determines a significant variation of its odor activity value and the imbalance of the original aroma composition.¹³¹

Odor and volatile organic compound emissions from polypropylene composites were investigated as a function of the zeolite type and content.¹³² The thermal stability and degradation temperature of the composites were slightly increased with increasing natural and synthetic zeolite content.¹³² At natural and synthetic zeolite contents of 3%, the various odors and VOC emissions from polypropylene composites were significantly reduced because of the absorption of the odor and VOC materials in the pore structures of the natural and synthetic zeolites.¹³²

High melt flow rate polypropylene is commonly produced by adding peroxide to the polymer, but such polypropylene usually has odor issues and also some of its physical properties are sacrificed.¹³³ Production of reactor-grade high melt flow rate polypropylene becomes necessary to avoid these issues.¹³³

A polymer composition comprising a heterophasic propylene copolymer, a mineral filler, and a light stabilizer comprising a fatty acid derivative and a benzoate derivative was developed.¹³⁴ The polymer composition is useful for automotive articles because the undesired effect of the final odor is reduced significantly compared to automotive articles comprising conventional light stabilizers.¹³⁴

8.29 POLYSTYRENE

For food contact applications, it is desirable to have low monomer concentration to prevent odor and taste transfer to food stored in the polystyrene containers.¹³⁵ Common commercial polystyrene has a residual styrene content of 500-700 ppm by weight.¹³⁵ With the use of higher than normal vacuum, this concentration can be brought down to 200-300 ppm.¹³⁵ The anionic polymerization, in batch or plug flow reactor, may give levels of 10-20 ppm, and has theoretical capability to produce polystyrene with 1 ppm styrene content.¹³⁵ Monomer can also be formed by thermal degradation of oligomers (especially dimers and trimers), therefore, their level should also be kept low to prevent the transfer of monomer to food products.¹³⁵ This can be achieved by anionic polymerization.¹³⁵

Odor can be reduced by addition of adsorbent clay.¹³⁶ Clay concentration is in the range of 0.1 to 10 wt%.¹³⁶ In addition to styrene, butadiene dimer, present at low levels, has been identified as a significant source of odor in styrene-maleic anhydride polymer containing resins.¹³⁶ The resin composition is useful for molded articles and foam.¹³⁶

γ -Irradiation of polystyrene only causes observable changes in odor and taste transfer to water at high radiation doses (60 kGy) which are only used in the special-purpose sterilization.⁹⁹ Polystyrene is the second most resistant polymer after poly(ethylene terephthalate) out of six tested packaging materials.⁹⁹

Three grades of polystyrene (titanium dioxide tinted, containing an additional layer of aluminum oxide, and containing, in addition, carbon black) were used for packaging of sour cream.¹³⁷ Packaged sour cream was exposed to UV radiation for 36 hours to simulate its exposure on store shelves.¹³⁷ Incorporation of a layer of carbon black as a light barrier in the packaging material protected the sour cream from degradation when exposed to light in this experiment.¹³⁷

The study found no evidence among industry workers that current or historical exposure to styrene can be associated with impairment of olfactory function.¹³⁸ Elevation of styrene odor detection threshold among exposed workers indicated exposure-induced adaptation.¹³⁸

A polymer article having odor absorption capabilities contains activated carbon particles encapsulated with a non-water soluble amorphous polymer.¹³⁹ The non-water soluble amorphous polymer is incompatible with the matrix polymer.¹³⁹ Polystyrene is used as encapsulation polymer.¹³⁹

8.30 POLYSULFIDE

The mercaptan-terminated polymers impart strong odor, which limits the practical utility of these polymers.¹⁴⁰ (Vinylaryl)alkyl-terminated polysulfides have similar properties to mercaptan-terminated polymers but have no odor.¹⁴⁰ The invention regards modification of epoxy resin with (vinylaryl)alkyl substituted polysulfide.¹⁴⁰ The resin has no objectionable odor even if heated to 125°C.¹⁴⁰

A conventional process of producing polysulfide includes the reaction of di-t-dodecyl polysulfide with t-dodecylmercaptan in the presence of a catalyst.¹⁴¹ Polysulfide produced in such a manner has some unreacted mercaptans and residual H₂S, which contribute to odor.¹⁴¹ In the invention, crude polysulfide is contacted with a metal salt of an acid (e.g., copper acetate) in the presence of a solvent (e.g., methanol and water).¹⁴¹ In this process, deodorized polysulfide is produced which has less than 30 ppm by weight of mercaptan sulfur, after at least 30 days of storage at 20-30°C.¹⁴¹

The high quantity of dichloro and polychloro compounds found in the heavy ends waste is useful for polymerization with alkaline polysulfide to form polysulfide polymer.¹⁴² But because of the presence of dihalides, this polymer has a strong odor.¹⁴² The invention shows how to refine heavy ends waste material prior to its use in synthesis to produce low odor polysulfide.¹⁴²

The process of production of low odor polysulfide, described in the invention, includes contacting mercaptan with elemental sulfur in the presence of a catalyst to produce an intermediate product.¹⁴³ The intermediate product is then contacted with carbon dioxide or carbon dioxide-generating compound in the presence of a catalyst which has base and surfactant.¹⁴³

The composition has polysulfide and inhibitor which reduces the odor of polysulfide.¹⁴⁴ The inhibitors are selected from a group consisting hydrocarbyl acrylates and methacrylates.¹⁴⁴

Polysulfide may contain an odor-masking agent, such as wintergreen, cinnamon, vanillin, terpenes, sesquiterpenes, and their combinations.¹⁴⁵ Polysulfide can also be deodorized by a small addition of tertiary alkanolamine (2.25-2.5 wt%).¹⁴⁶ Use of H₂S scavengers has also been proposed.¹⁴⁷ The scavenging agents are glycidyl ether compounds.¹⁴⁷

Analysis of polysulfides in a drinking water distribution system shows the presence of dimethylsulfide, dimethyldisulfide, and dimethyltrisulfide.¹⁴⁸ The presence of sulfide and polysulfides in drinking water distribution systems is of particular concern because these species consume disinfectants and dissolved oxygen, react with metal ions to produce insoluble metal sulfides, and can cause taste and odor problems.¹⁴⁸

Nitrate dosing is commonly used to control hydrogen sulfide production in sewer systems.¹⁴⁹ However, the quick rebound of the sulfide concentration after nitrate depletion has been observed and results in more serious odor and corrosion problem.¹⁴⁹ Indirect sulfur reduction *via* polysulfide contributes to a serious odor problem in a sewer receiving nitrate dosage.¹⁴⁹

A linear alkyl group 6 to 12 carbon atoms enables maintenance of the high sulfur content, good formation of a metal sulfide film on a metal surface, and a reduction in low molecular weight mercaptans that cause odor.¹⁵⁰

8.31 POLYURETHANE

Amine-boron composition for catalysis of urethane reaction, especially useful in foam production, have been designed to produce low odor polyurethanes.¹⁵¹ Catalyst can be prepared by mixing triethylenediamine with boric acid.¹⁵¹ The number of commonly used tertiary amine catalysts are relatively volatile and have unpleasant smell.¹⁵¹ Even at low levels, they may impart odor to the polyurethane formulation.¹⁵¹

Low odor flexible polyurethane foams are obtained by reaction of polyisocyanate with special polyetherol mixture.¹⁵² These foams are useful as carpet, upholstery, seat, and packaging materials, as well as in the hygiene sector.¹⁵² It was noticed that it is difficult to produce low-odor foams using ethylene oxide-rich polyetherols.¹⁵²

Commercially available soy polyols contain aldehydes and hydroperoxides that contribute to unpleasant odor of the soy-based polyurethane foams.¹⁵³ From previous experiences, it is known that odor can be masked by using fragrances or reduced by epoxidation.¹⁵³ Odor barrier layer is applied for encapsulation of cellular material to confine odors emanating from the cellular material.¹⁵³

Production of odorless polyol is described, which includes a stripping step to remove odorous substances. Polyurethane foams manufactured from this polyol can be used in cosmetic formulations.¹⁵⁴ Odors potentially come from non-reactive impurities that are present in polyisocyanate, polyol, and water.¹⁵⁴ In particular, polyols have a minute amount of volatile impurities that impart distinct odor.¹⁵⁴ Also, volatile amine catalysts can cause odor in foams.¹⁵⁴ Blowing agents are not reactive and volatile, so they can contribute significantly to the foam odor.¹⁵⁴ In odorless foam, CO₂ or water should be used as blowing agents.¹⁵⁴

VOC-free polyurethane coating of this invention uses imines to obtain a product having special advantage in indoor applications.¹⁵⁵ VOC-absorbing agent is included in formulation for polyurethane foam.¹⁵⁶ The common VOCs in polyurethanes include unused reactants from gelling and blowing reactions, carbon dioxide, stabilizers, antioxidants, inert blowing agents, fluorocarbons, chlorofluorocarbons, methylene chloride, acetone, trichloroethane, butylated hydroxylated toluene, trace impurities from raw materials, and other byproducts.¹⁵⁶ These VOCs give foam an offensive odor. VOC-absorbing agent may be zeolite or carbonaceous compound (e.g., carbon black, charcoal, activated carbon, graphite, etc.).¹⁵⁶

Polyurethane foams made from low odor polyols are disclosed.¹⁶¹ Examples of odor-producing compounds include lipid oxidation products, which are typically aldehyde compounds, such as hexanal, nonanal, and decanal.¹⁶¹

Several polyurethane materials used in automotive applications have been tested for their influence on odor, including floor acoustic insulation and roof lining (PU foam), and foam wires holder.⁴⁰ Principal component analysis and cluster analysis have been used in order to classify and identify the odors coming from the parts under study.⁴⁰ Good separation among odors of samples of comparable composition has been obtained using the first coefficients of the fast Fourier transform of the whole curve as the input variable of principal component analysis.⁴⁰ These results show the feasibility of the conducting polymer array of sensors to discriminate odors for the air cabin quality control.⁴⁰

The aromatic diamine curative, Ethacure 300, has greatly reduced the odor of the liquid product, which is used in both hot and room-temperature polyurethane cast elastomers and sealants.¹⁵⁷

Wound dressings are designed to facilitate fast healing and dealing with odor, leakage, maceration, pain, infection, and other problems for wounded patients.¹⁵⁸ The functional wound dressings include alginate, chitosan, hydrogel, hydrocolloid, and polyurethane-based products.¹⁵⁸

Spray polyurethane foam has become a popular form of home insulation in the United States, but there have been adverse health effects reported by home owners.¹⁵⁹ Fishy odors were reported and acute watery and burning eyes, burning nose, sinus congestion, throat irritation, cough, dyspnea and chest tightness were developed.¹⁵⁹ Analysis of indoor air and headspace gas from the foams showed increased concentrations of VOCs derived from spray polyurethane foam and common indoor air pollutants.¹⁵⁹ The levels of VOCs decreased after spray polyurethane foam was completely removed.¹⁵⁹

A reactive formulation of a flame resistant flexible polyurethane foam with reduced odor was developed.¹⁶⁰ It is particularly suited for use in under-the-hood vehicle applications which require sound deadening and vibration management.¹⁶⁰ Odor can be a problem for flame-retardant foam, containing certain additive-type flame-retardant components.¹⁶⁰ An odor reducing additive, such as a non-halogen containing copper compound was used in the developed product.¹⁶⁰

8.32 POLYVINYLACETATE

Low odor, dry polyvinylacetate particles are produced from vinyl acetate monomer-free polymer.¹⁶¹ The resulting polyvinylacetate dispersions are low in odor, producing clear, dry films that may be used in adhesives, sealants, caulks, and coatings.¹⁶¹ Polymer that contains less than 50 ppm monomer is considered in the USA as monomer-free.¹⁶¹ If product contains 0.1 wt% monomer, a warning statement must appear on the material safety data sheet.¹⁶¹ The product of this invention is dried to remove free monomer from particulate product, which may then be used for redispersion.¹⁶¹ Drying temperature should not exceed fusion temperature of polyvinylacetate (about 93.3°C) because particles will coalesce and become fused together, which will hamper their redispersion.¹⁶¹ Typically, spray drying at temperature of 82.2°C is used.¹⁶¹

8.33 POLYVINYLALCOHOL

Proton acceptor is mixed with polyvinylalcohol before it is subjected to thermal degradation.¹⁶² This renders odor-free material after it was thermoformed.¹⁶² Thermoforming

without stabilization leads to product discoloration and odor associated with acetic acid.¹⁶² Suitable proton acceptors include zinc oxide, calcium carbonate, sodium bicarbonate, polyvinylpyridine, polyvinylpyrrolidone, and many other additives.¹⁶²

Odor-free multilayer products have been produced by a close control of processing parameters such as temperature, flow rate, and pressure.¹⁶³

Fragrances are added to extruded polyvinylalcohol.¹⁶⁴ Product is used for fabrication of toilet rim blocks or effective air freshening devices.¹⁶⁴

Polyvinyl alcohol emulsions are susceptible to biodeterioration depending on the presence of nutritional components.¹⁶⁵ Polyvinylalcohol emulsions are susceptible to bacterial, yeast, and fungi.¹⁶⁵ Some surfactants, wetting agents, defoamers, and thickeners used in these emulsions make them vulnerable to the microbiological attack.¹⁶⁵ Plant hygiene and presence of biocides impacts their vulnerability.¹⁶⁵ The following bacteria have been isolated from emulsions: *Achromobacter* sp., *Acinetobacter* sp., *Alealigenes* sp., *Arthrobacter* sp., *Bacillus* sp., *Citrobacter freundii*, *Corynebacterium* sp., *Enterobacter cloacae*, *Enterobacter* sp., *Escherichia coli*, *Flavobacterium* sp., *Klebsiella pneumoniae*, *Lactobacillus* sp., *Micrococcus* sp., *Proteus mirabilis*, *Proteus rettgeri*, *Proteus* sp., *Proteus vulgaris*, *Providencia alcalifaciens*, *Providencia rettgeri*, *Pseudomonas aeruginosa*, *Pseudomonas cepacia*, *Pseudomonas fluorescens*, *Pseudomonas maltophilia*, *Pseudomonas putida*, *Pseudomonas* sp., *Sarcina luteus*, and *Serratia marcescens*.¹⁶⁵ The following fungi and yeasts have been isolated from emulsions: *Aureobasidium* sp., *Alterriaria* sp., *Aspergillus* sp., *Bimorphic fungus*, *Candida boidinii*, *Cladosporium* sp., *Filamentous fungus*, *Fusarium* sp., *Geotrichum candidum*, *Geotrichum* sp., *Penicillium* sp., *Pichia* sp., *Rhodotorula rubra*, *Saccharomyces* sp., *Torula* sp., and *Torulopsis* sp.¹⁶⁵

Microbiological growth in emulsion causes viscosity and pH changes, production of odors, enzyme production, visible surface growth, and color change.¹⁶⁵

Anti-insect packaging films containing cinnamon oil encapsulated by polyvinylalcohol for repelling *Plodia interpunctella* (Hübner) larvae were manufactured.¹⁶⁶ The microcapsule emulsion of cinnamon oil and PVA was printed onto polypropylene film in form of ink using the gravure printing method.¹⁶⁶ Antimicrobial-coated polypropylene films with polyvinylalcohol was used in packaging of fresh beef.¹⁶⁷ Surface coating did not affect natural flavors of the product.¹⁶⁷

8.34 POLYVINYLBUTYRAL

Polyvinylbutyral has been produced, which has a low odor during production and handling.¹⁶⁸ Low odor polyvinylbutyral is produced by extrusion of moisture-containing polymer in an extruder equipped with devolatilization section having at least one vent portion.¹⁶⁸ Polyvinylbutyral pellets produced in this way have a concentration of butyl aldehyde and 2-ethyl-2-hexenal of 100 ppm or less.¹⁶⁸

A polyvinylbutyral resin pellet is produced that gives reduced odor when produced and handled, as well as has a high apparent density and favorable handleability.¹⁶⁹ When water content is adjusted to 6 wt% or less, devolatilization of butyl aldehyde and 2-ethyl-2-hexenal occurs and odor of the polyvinylbutyral resin pellet can be reduced.¹⁶⁹

8.35 POLYVINYLCHLORIDE

Table 8.4 gives the lists of odor producing chemicals from different sources.

Table 8.4. Odor-related compounds found in different sources.¹⁷⁰⁻¹⁷²

Environment	Odorants
water pipe, licheates	2-methylcycloheptane, 2-methylcyclopentanone, methylester of 2-octanoic acid, 2-(2,4-dichlorophenoxy)-N,N-dimethylacetamide, 1-thio, S-sec-butyl ester of acetoacetic acid, 4-nitrobenzofuran, 4, (1,1-dimethyl) cyclohexanol, 1-[(2,2-dimethyl-1,3-dioxalan-4-yl) methoxy] 2-heptadecanone, oxime of cyclopentanone, 3-hydroxybenzaldehyde, 2,5-dichloro-3,6-dimethyl, methyl ester of benzoic acid
automotive industry	methyl isobutyl ketone, toluene, N,N-dimethyl-formamide, phenol, 2-ethyl-1-hexanol, 3,4-dihydro-3-vinyl-1,2-dithiin, 2,3,5-trimethylbenzene-1,4-diol, tri-decan, quinoline-derivative
flooring & adhesive	2-ethyl-1-hexanol, 2-ethylhexyl acetate, acetic acid, methacrylic acid, acetate
building materials	2-ethyl-1-hexanoic acid, 2-ethyl-1-hexanol, n-butanol, 2-butanol, 1-chloropropanol, 1,2-dichloropropane

A study of the production of odor-causing compounds was conducted from the leaching of polyvinylchloride pipe and its joints, primer and cement, into drinking water distribution systems (Table 8.4).¹⁷⁰ It is clear from the list that these compounds are not from PVC but rather from primer and adhesive.¹²⁶ Flavor profile analysis shows that pipe alone has very low odor intensity (0.8) as compared with pipe+primer+cement (4).¹⁷⁰ The following odor descriptions are associated with the odorants in Table 8.4 (first row): sweet, phenolic, medicinal, and earthy.¹⁷⁰

Volatile organic compounds emitted from three PVC skin samples also called coated plastic tissues, were studied by means of an electronic nose, olfactory sensory analysis, and GC/MS analysis.¹⁷¹ All studied products are fabricated for Renault cars.¹⁷¹ Only 2-ethyl-1-hexanol may be a product of degradation of plasticizer used in production, the remaining components are part of the coating.¹⁷¹ The following descriptions of odors were detected by Renault panelists: amine, sulfured, roasted, phenolated, balsamic, honeyed, fatty, fruity, ethereal, esterified, animal, earthy, and musty.¹⁷¹

2-Ethyl-1-hexanol is detected in indoor air at relatively high concentrations.¹⁷² Moisture with a high pH in concrete slabs and self-leveling sub-flooring material reacts with di-2-ethylhexyl phthalate, the plasticizer of polyvinylchloride flooring and compounds containing the 2-ethyl-1-hexyl group in the adhesive.¹⁷² 2-Ethyl-1-hexanol is considered to be one of the causes of odor in the indoor air and sick building syndrome.¹⁷² Other odor components are produced by acrylic adhesives used with flooring.¹⁷²

Secondary emissions from building materials found in indoor air are products of degradation of a thermal stabilizer, plasticizers, and flame retardants.¹⁷³ Among building materials, PVC is a minor contributor of indoor pollution.¹⁷³

VOC detected in the test water from PVC pipes contained hexanal, octanal, nonanal, and decanal.⁸⁷ Only trace amounts of hexanal and octanal were found in the test waters,

whereas nonanal and decanal were present in concentrations from 280 ng/l or less and 170 ng/l or less, respectively.⁸⁷

Hydrogen sulfide is produced by the microbial breakdown of organic matter.¹⁷⁴ This anaerobic process mainly takes place in the sediments and biofilms covering the wetted pipe surfaces.¹⁷⁴ The gas-phase hydrogen sulfide concentration in concrete sewers typically amounts to a few percent of the equilibrium concentration calculated from Henry's law.¹⁷⁴ In the plastic pipe (PVC and HDPE) sewers, significantly higher concentrations of hydrogen sulfide were predicted because of the slower adsorption and oxidation kinetics on such surfaces.¹⁷⁴

8.36 POLYVINYLCHLORIDE, CHLORINATED

Pipes constructed from chlorinated polyvinylchloride are commonly used in drinking water distribution systems and premise plumbing.⁹¹ The effects on odor, organic chemical release, trihalomethane formation, free chlorine demand and monochloramine demand were determined for water exposed to cPVC pipes.⁹¹ cPVC pipe leached more TOC and had higher disinfectant demand than glass pipe (control).⁹¹ 1,3-Butadiene was found to cause gasoline-like odor in cPVC pipe.⁹¹

8.37 POLYVINYLPYRROLIDONE

Polyvinylpyrrolidone films containing different pH indicators (methyl orange, methyl red, thymol blue, phenol red, phenolphthalein, and alizarin yellow) were exposed to methanol and composition of odor components of citrus fruits.¹⁷⁵ Changes in color were observed.¹⁷⁵ These color images were scanned, separated to red, green, and blue components, and then converted to gray levels.¹⁷⁵ It was possible to distinguish between exposures to different odors, therefore this method can be used to determine odor.¹⁷⁵

Biomimetic extracellular matrix micro/nanoscale fibers based on polyglycolic acid, polylactic acid, polyacrylic acid, poly-ε-caprolactone, polyvinylpyrrolidone, polyvinyl alcohol, polyethylene glycol, exhibit *in vivo* and *in vitro* wound healing properties and enhance re-epithelialization.¹⁷⁶ They protect peri-wound skin, maintain a suitable moisture at the wound level, prevent and keep under control microbial biofilms, cleanse the injured tissues, eliminate/minimize pain, remove dead spaces and nonviable tissues, control the odors.¹⁷⁶

8.38 RUBBER

It was discovered that the addition of zinc dust initiates a reaction with hydrogen sulfide, which removes major odorant of rubber.¹⁷⁷ Similar result can be obtained with the addition of lead carbonate, which also can react with hydrogen sulfide.¹⁷⁷

Odor masking was suggested for rubber products.¹⁷⁸ Some accelerators impart an objectionable odor to the finished goods.¹⁷⁸ Addition of perfumes eliminated the problem with odors.¹⁷⁸ The aromatic substances suggested for odor masking included geraniol, citronellol, linalool, cinnamic alcohol, anisic alcohol, methyl phenyl carbinol, terpeneol, borneol, phenyl ethyl alcohol, and phenyl propyl alcohol.¹⁷⁸ Some of them (phenyl ethyl alcohol and phenyl propyl alcohol) have accelerating properties on a cure.¹⁷⁸

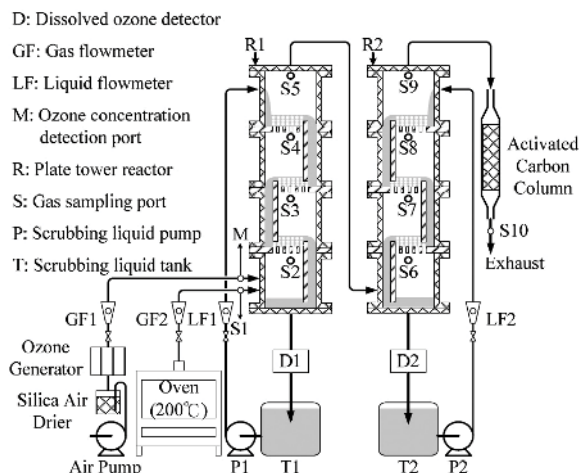


Figure 8.6. Schematic diagram of rubber ozonization system.
 [Adapted, by permission, from Perng C-H, Cheng I-L, Wang I-C, Chou M-S, *Aerosol Air Quality Res.*, 11, 51-58, 2011.]

The removal of odorous compounds in gasses emitted from rubber processing industries is accomplished by ozonization.¹⁸¹ Figure 8.6 shows a schematic diagram of a rubber ozonization system which was used for elimination of odor.¹⁸¹ The system consists of an ozone generator, an electrical-heated oven, two sieve-plate columns connected in series, two water circulation pumps, and the associated pipes, and a granular activated carbon column.¹⁸¹ Each sieve-plate column was partitioned into four 1-L compartments of equal dimensions with 3 sieve plates.¹⁸¹ Each sieve plate has 64 holes of 1 mm in diameter to enhance the contact of ozone and the influent odorous gas when performing dry-ozonation.¹⁸¹ VOC compounds from heated rubber contained the following components: 1,1-dichloroethylene, isopropylbenzene, 1,2,4-trichlorobenzene, sec-butylbenzene, 1,3-dichlorobenzene, hexachlorobutadiene, and naphthalene.¹⁸¹ Wet oxidation gave better performances than the dry ozonization.¹⁸¹ The wet ozonization gave 97 and dry ozonization gave over 90% removal of VOCs and odorous intensity removal, respectively, with the operation conditions of an initial ozone concentration of 4.0 ppm.¹⁸¹ Activated carbon was effective for both physical and chemical removal of residual VOCs, odorous compounds, and ozone in the effluent gas from the ozonation system.¹⁸¹

8.39 SILICONE

A process for preventing odor in a polyoxyalkylene group-containing polyorganosiloxane comprising addition of phytic acid during and/or after production has been invented.¹⁸² The amount of phytic acid used is in the range of 50 to 500 ppm, based on polyorganosiloxane.¹⁸²

Cured silicone is inhibited from evolving unpleasant odors with a passage of time.¹⁸³ The surface of cured silicone is treated with an alkali, by dipping the cured silicone powder in aqueous alkaline solution.¹⁸³ The unpleasant odor is a result of oxidation of surface

The invention is related to the production of foamed synthetic rubber latex sponge, which has improved odor characteristics.¹⁷⁹ Also, natural rubber latex sponge has a protein-like odor.¹⁷⁹ It has been discovered that polybutadiene latex may be used for the production of foamed latex sponge, which has improved odor characteristics.¹⁷⁹

The natural rubber is modified with a polar group-containing monomer.¹⁸⁰ The odor produced in mastication is decreased due to modification.¹⁸⁰ Modification monomer is used in an amount of 0.2-1 wt%. A number of suitable monomers are discussed in this invention.¹⁸⁰

organic groups and oxidation of components presents in the cured material.¹⁸³ The oxidation is induced by UV and temperature.¹⁸³ These reactive groups are neutralized and decomposed by treatment with alkali.¹⁸³ Alkali metal, alkaline-earth metal salts of inorganic acids, alkaline-earth metal hydroxides, ammonia, and many other alkaline compounds can be used in the invention.¹⁸³

A silicone rubber composition that does not foam and produce odor has been patented.¹⁸⁴ It contains polyorganosiloxane, microparticulate silica, bis-(ortho-methylbenzoyl) peroxide, and bis-(para-methylbenzoyl) peroxide.¹⁸⁴

Curable composition contains carboxylic acid-scavenging reactant with an amount sufficient to reduce odor associated with silicone curing.¹⁸⁵ The carboxylic scavenging reactant included carbodiimide in a form of monocarbodiimide or polycarbodiimide, an aziridine, or their combinations.¹⁸⁵

Prolonged action of flavors and fragrances is achieved by encapsulation of an active fragrance ingredient into a polymer matrix, the formation of complexes, or the use of covalent anchoring to the matrix.¹⁸⁶ Different organosilicone carriers were covalently bonded with model fragrant systems.¹⁸⁶ They can be released by acidic or basic hydrolysis.¹⁸⁶

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ODOR IN VARIOUS PRODUCTS

9.1 ADHESIVES

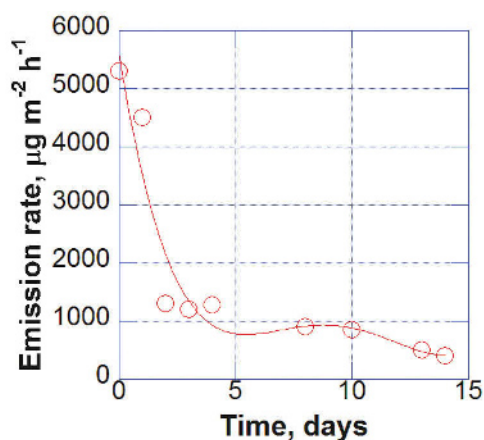


Figure 9.1. 2-Ethyl-1-hexanol emission from acrylic adhesive. [Data from Chino S, Kato S, Seo J, Ataka Y, *Bldg. Environ.*, **44**, 1337-1342, 2009.]

of the copolymer used in the production of adhesive.¹ It can be noticed that the emission rate decreases rapidly with time.¹

Odor from packaging adhesive remains within the package.² All adhesives have an odor, even though the adhesive industry has greatly reduced the offensiveness of adhesive odors.² Water-based adhesive containing poly(vinyl acetate) was used in this invention as a low odor adhesive.²

Acrylates and methacrylates are known to have offensive odors.³ Low odor adhesive composition of the invention contains methacrylates having urethane groups.³ The patent contains information on the method of their production.³ Still another technology is proposed for the production of methacrylate adhesive which contains rubber block copolymer. Methyl methacrylate ester is the major component of the adhesive. It does not produce a strong odor, unlike C₁-C₄ methyl methacrylates which are very volatile and have a strong odor.

Multifunctional adhesive food wraps contain chemical means that can be used to eliminate the odor of adhesive.⁵ Chemicals involved include sodium bicarbonate, potassium permanganate, cyclodextrin, zeolites, molecular sieves, activated carbon, zinc oxide, chitosan, silica gel, and polyalkylene imines.⁵ Chemically reactive materials are generally

Decomposed chemicals of esters contained in adhesives for PVC flooring have been the subject of an investigation looking at the reasons for sick building syndrome.¹ Several adhesives are used in buildings for this purpose, including styrene-butadiene rubber and various acrylic resins.¹ The following compounds were emitted from adhesives: 2-ethylhexyl-acrylate, 2-ethylhexyl methacrylate, and 2-ethylhexyl acetate, 2-ethyl-1-hexanol, acetic acid, methacrylic acid, propylene glycol mineral spirit, polyglycol, terpene, and texanol.¹ These compounds contribute to odor. Figure 9.1 shows the rate of emission of 2-ethyl-1-hexanol from the acrylic adhesive, which is formed as a product of hydrolysis

basic in nature to neutralize more acidic target gasses.⁵ The odor absorbing materials can be incorporated into film structure. The film may absorb odors from inside and outside the package.⁵

Light odor, light color, hot pick-up adhesive has been invented.⁶ It is made from hydrogenated tackifying resin combined with waxes, oils, stabilizers, and other additives.⁶ Frequently, hot melt adhesives use rosin as basic material.⁶ Rosin is naturally derived material that causes severe allergic reactions and contains many low molecular materials that are volatile and cause smoke and odor at application temperatures.⁶ Hydrogenated synthetic hydrocarbon resins contain relatively small amounts of volatile compounds, do not produce smoke, and do not cause odor problems.⁶

Twenty-five compounds were detected in adhesives used in food packaging laminates.⁷ Seventy-six percents of these compounds migrated into a dry food simulant.⁷ Acetic acid, butyric acid and cyclohexanol with vinegar, cheese, and camphor odors were the most abundant.⁷

The main disadvantages of marine acrylic adhesives are that they are flammable in the uncured state and have a characteristic acrylic monomer odor.⁸ In applications of acrylic adhesives in the wood products, the main disadvantages are an odor, higher cost, and limited durability.⁹

9.2 AEROSPACE

Curable polythiol-cyclopolyene sealant compounds have been developed for the aerospace industry.¹⁰ Thiol-terminated polymers have a long history of use in aerospace because of their fuel resistant nature upon crosslinking.¹⁰ Suitable catalysts for the reaction of polythiol and cyclopolyene include azo or peroxide-free radical initiators, such as azobisalkalenitrile, produced by DuPont, because of their desirable activation temperatures and low level of residual odor.¹⁰ Suitable thiols include dimercaptodiethyl sulfide and dimercaptodioxaoctane because they produce odorless polymers when reacted with vinylcyclohexene or dipentene.¹⁰

Combination of polythiol, polyepoxide, and polyvinyl ether is used for the production of aerospace sealant.¹¹ The resin obtained according to this invention had a mild odor.¹¹

9.3 ALCOHOLIC BEVERAGES

Conductive multiwall nanotube-polymer two-layer composite inspired by the structure of the olfactory system was designed for analysis of alcoholic beverages.¹² Through a combination of conducting MWNTs and a sensing polymer, this material provided enhanced sensitivity, making it highly suitable as a microarray gas-sensing element.¹² To use carbon nanotube-polymer composites as gas sensors, a short recovery time is required.¹² The interaction between the gas and polymer membrane is usually reversible physical absorption bonding.¹² There are five kinds of physical absorption bonding: hydrogen-bond acidic, hydrogen-bond basic, dipolar and hydrogen-bond basic, moderately dipolar and weakly hydrogen-bond basic or acidic, and weakly dipolar with weak or no hydrogen-bond properties.¹² Eight polymers were selected for short recovery time sensors: styrene/allyl alcohol copolymer, polyvinylpyrrolidone, poly(vinylidene chloride-co-acrylonitrile),

poly(methyl vinyl ether-alt-maleic acid), poly(α -methylstyrene), hydroxypropyl methyl cellulose, poly(ethylene adipate), and poly(vinyl benzyl chloride).¹² The portable electronic nose based on the above sensors and principles successfully identified four complex alcohol vapors, such as sake, sorghum liquor, medical liquor, and whiskey.¹²

Many terms describe the characteristic tastes and flavors of sake, including ethyl caproate flavor, fatty odor, sweet caramel-like odor, roast odor, hineka odor, raw-hineka odor (similar to mureka odor), yeast-debris odor, sulfur compound odor, diacetyl odor, umami taste, bitterness, and astringent taste.¹⁶ These organoleptic properties are formed by different concentrations and combinations of the chemical compounds in the sake.¹⁶ For example, 49 chemical compounds were tested for their correlation with the pleasant bitter taste of sake.¹⁶

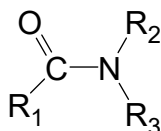
2,4,6-Trichloroanisole is a microbial metabolite formed from chlorophenols through the activity of several natural fungal strains present on the cork made out of oak bark.¹³ It is the primary compound responsible for the musty/mold off-odor known as “cork taint” present in cork stoppers, wine, water and alcoholic beverages.¹³ A rapid, novel biosensor system was developed for the purpose of studies of “cork taint”.¹³ The developed sensor had higher sensitivity than the human sensory threshold.¹³ In addition, the assay was quite selective against other haloanisoles and halophenols structurally related to or co-occurring with 2,4,6-trichloroanisole.¹³

Comprehensive two-dimensional gas chromatography combined with time-of-flight mass spectrometry was used to identify odor-active compounds which were undetermined after the chromatographic separation.¹⁴ Ethyl 2-methylbutanoate, 2-phenylethanol, ethyl butanoate, ethyl 2-methylpropanoate, ethyl hexanoate, oct-1-en-3-one, 2-phenylethyl acetate, ethyl dodecanoate, 3-methyl-1-butanol, and 2-methylbutanoic acid were among the most potent odorants in two ciders.¹⁴

Application of gas chromatography-olfactometry in analysis and quality assessment of alcoholic beverages has been discussed in a review paper.¹⁵ The paper contains information on sample preparation methods, factors influencing results, quantitative methods, and examples of application.¹⁵

9.4 AGRICULTURE

Low odor, low volatility solvent for agriculture has been proposed.¹⁷ The solvent is an amide having the following composition:¹⁷



where:

- R₁ C₃ to C₁₅ hydrocarbon group
- R₂ C₁ or higher hydrocarbon group
- R₃ C₁ or higher hydrocarbon group

Solvents are used in agriculture in the preparation of agricultural formulations, for example, in pesticide products.¹⁷

Anaerobic digestion produced useful fertilizers, i.e. the digestate.¹⁸ Digestate misuses led to odors and ammonia emission.¹⁸ Subsurface injection of digestate reduced greatly odors and NH₃ emissions (69 and 77%, respectively).¹⁸

An odor mitigating agricultural fumigant includes a mixture of dimethyl disulfide and 1,3-dichloropropene, which is added to the mixture as an ingredient of Telone[®] or Telone II[®].¹⁹ This mixture significantly reduces the mercaptan-like odor that normally accompanies Paladin[®] (dimethyl disulfide) and Paladin[®] based mixtures.¹⁹

The invention outlines a process for reducing ammonia loss and odor from organic material or waste to the atmosphere.²⁰ A plasma generator is applied to upgrade organic waste and manure with a mixture of acidic nitrates and nitrites.²⁰

9.5 AUTOMOTIVE MATERIALS

Electronic nose based on chemoresistive polymeric sensors was used for the discrimination of eight sample materials used in the car manufacture, including parts fabricated from polyurethane.²¹ Principal component analysis and cluster analysis have been used in order to classify and identify the odors.²¹ Good separation among odors of samples of comparable composition has been obtained using the first coefficients of the fast Fourier transform of the whole curve as the input variable of principal component analysis.²¹

Smell and fogging caused by automotive parts from different polypropylene grades have been studied by thermodesorption and static headspace with subsequent GC/MS analysis, as well as fogging analysis.²² Only alkanes and alkenes with a chain length higher than C₁₆ were present in the fogging residue.²² Hydrocarbons with a shorter chain length were not causing any fogging problems. It was also found that thermodesorption emission depended on sample surface rather than on sample mass.²²

Odors of new cars are important today for the consumers' comfort.²³ Interior trim manufacturing process and use of petrochemical compounds cause many rubbers and foams used in automotive materials to result in a "new car odor" mostly enjoyed but sometimes felt as unpleasant by customers.²³ The odors of several PVC skins for Renault cars were tested by human assessors.²³ The volatile organic compounds were characterized by electronic nose and their identification was carried out by GC/MS analysis.²³ The following chemical compounds were emitted from PVC skins: methyl isobutyl ketone, toluene, N,N-dimethylformamide, cyclohexanone, 2-ethyl-1-hexanol, 3,4-dihydro-3-vinyl-1,2-dithin, 2,3,5-trimethylbenzene-1,4-diol, tridecane, and quinoline derivative.²³

Ventilating device for an automotive vehicle has a filter to prevent accumulation of odors.²⁴ Odors may come from the inside of the vehicle, such as tobacco smoke, but also from the outside.²⁴ Activated carbon filter removes the odors from the atmospheric air.²⁴ Also, carbon paper is used to remove odors from both internal and outside air.²⁴ The use of activated carbon fibers in paper-like form permits the removal of offensive odor when the rear seat air conditioning system is operated with internal air.²⁴

A filter system was designed to remove the odor of diesel.²⁵ Fresh air supplied to the interior of the vehicle is filtered by the activated carbon filter designed for removal of diesel smell.²⁵ Crude diesel exhaust has more than 4,000 odor units as determined according to DIN 13725 and only 500 odor units when it is passed through the filter.²⁵ Activated carbon is impregnated with substances which eliminate acidic gasses.²⁵

A mist generating device has been developed which helps in elimination of microbial growth and preventing odors in vehicles.²⁶ Biological reaction-related odors in a vehicle are annoying, and, in some cases, they may become a health risk.²⁶ The source of odors involves bacteria, fungi, and other microorganisms.²⁶ This smell is felt when the air conditioner is turned on.²⁶

Automotive climate control system and method for exhaust odor abatement have been invented.²⁷ During acceleration, the air conditioning system works in recirculation mode because a high concentration of odor substances is expected in exhaust.²⁷ The system operates in fresh air mode when the probability of a high concentration of exhaust odors does not exist.²⁷ It is also possible that an odor detection system is involved which shuts off the external air when the odor is detected.²⁷

Some of the currently available anti-scratch additives can cause visible blooming, haze, surface stickiness or odor issues.²⁸ Chinaplas 2015, of IncoMold™K as a specialty additive for improved scratch resistance in high-quality automotive molded parts.²⁸

A polymer composition includes a heterophasic propylene copolymer, a mineral filler, and a light stabilizer based on a fatty acid derivative and a benzoate derivative.²⁹ Automotive articles are produced with reduction of the undesired odor as compared to automotive articles comprising conventional light stabilizers.²⁹

9.6 BOTTLES

Refillable poly(ethylene terephthalate) bottles are known to interact with chemicals.³⁰ Aroma compounds can be absorbed by the bottle material, remain after washing, and remigrate when the bottle is reused, resulting in off-flavor of the new product.³⁰ The poly(ethylene naphthalate) material exhibited significantly superior inertness properties, with only 3–24% of the aroma transfer properties of poly(ethylene terephthalate).³⁰ PET released organic contaminants into military package water and residual disinfectant generated trihalomethane contaminants.³⁴

Mineral water and soft drinks with off-odor were analyzed to identify contaminants originating from the previous misuse of the refillable poly(ethylene terephthalate) bottle.³¹ Substances responsible for the organoleptic change were 2-methoxynaphthalene, dimethyl disulfide, anethole, petroleum products, ethanol with isoamyl alcohol, and a series of ethers. The moldy/musty odor was caused by trichloroanisole.³¹ The origins of the off-odors were from previous consumer misuse of food products (liquorice-flavored alcohol, home-made alcohol containing fusel oil) or non-food products (cleaning products, petroleum products, oral moist snuff and others).³¹

Milk was stored in cardboard containers (control) and PET bottles with different protection against UV.³² The shelf life of milk was 10–11 days for both samples packaged in clear PET + UV absorber bottles and in cardboard containers.³² This is interesting considering that oxygen transmission rate of cardboard is 34.5 ml/package day atm, compared with only 0.77–0.85 ml/package day atm for different PET bottles.³² This shows that protection against UV is very important for the preservation of original milk odor.³²

PET was the most ionizing-radiation-resistant material, while the HDPE monolayer and multilayer showed some degradation after 60 kGy.³³ PS was slightly affected after 30 kGy, whereas PP was severely degraded and became very brittle.³³ Odor and taste transfer were observed with most plastics, especially at higher doses.³³

9.7 CEMENTITIOUS MATERIALS

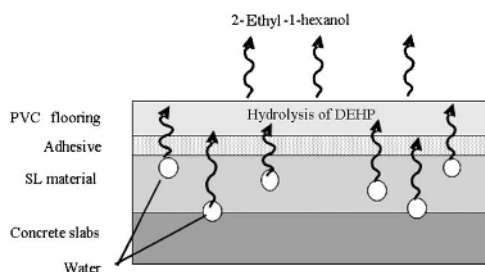


Figure 9.2. Mechanism of emission of 2-ethyl-1-hexanol from PVC flooring. [Adapted, by permission, from Chino S, Kato S, Seo J, Ataka Y, *Bldg. Environ.*, 44, 1337-42, 2009.]

Figure 9.2 shows the mechanism of emission of 2-ethyl-1-hexanol from PVC flooring adhered to concrete slabs.³⁵ It has been reported that building dampness in concrete floor constructions, with the emission of 2-ethyl-1-hexanol, is related to sick building syndrome symptoms, although indications of microbial growth and water leakage in the building were not found.³⁵ Indoor air pollution with 2-ethyl-1-hexanol has been identified not only in Europe but also in Japan.³⁵ It has been reported that 2-ethyl-1-hexanol has been measured at high concentrations

(above 400 mg/m³) in the indoor air over the long term.³⁵ 2-Ethyl-1-hexanol is primarily emitted from the floor.³⁵ PVC materials include di-2-ethylhexyl phthalate as a plasticizer.³⁵ Di-2-ethylhexyl phthalate is an ester of phthalic acid and 2-ethyl-1-hexanol.³⁵ The cause of 2-ethyl-1-hexanol emission from PVC material is the hydrolytic degradation of esters yields alcohols and acids under acidic or alkaline conditions.³⁵ Di-2-ethylhexyl phthalate included in the PVC flooring material is hydrolyzed under alkaline conditions derived from the concrete slabs and self-leveling sub-flooring materials that contain cement.³⁵

The odors emitted from three building materials such as white cedar, tatami and concrete were detected.³⁶ The acceptability of the concrete odor was low.³⁶

Hydrogen sulfide absorption and oxidation by corroding concrete surfaces were quantified.³⁷ Hydrogen sulfide was identified as the cause of the sulfuric acid and consequently of the concrete corrosion.³⁷ Significant corrosion rates—several millimeters of concrete per year—can potentially occur at hydrogen sulfide gas phase concentrations well below 5–10 ppm.³⁷

Indoor pollution was caused by emitted ammonia from concrete in a newly built office in Beijing.³⁸ An increased indoor concentration of ammonia (3–6 ppm) and benzene (26.8 µg/m³) was measured in the indoor air in the Beijing office.³⁸ The probable source of ammonia was traced to additives in the concrete.³⁸

9.8 COATED FABRICS

Early fabrics coated with rubber were only used in industrial applications in which their characteristic odor was not objectionable.³⁹ These included balloon bags, diaphragms, gaskets, conveyor belts, tire cord, inflatable life rafts, pontoons, and the like.³⁹

Antimicrobial finishes are one of the fast-developing innovations. Performance apparel represents one of the most dynamic sectors.⁴⁰ Antimicrobial finishes increase the microbiological resistance of protective garments.⁴⁰ Tents and shelter fabrics are subjected to microbial degradation in use and storage.⁴⁰ Effective biocidal treatments prevent mildew and odor formation.⁴⁰ The functionalized silane dendrimers of this invention may be

applied by bath during the production process or by spray as post-production finish. In both cases, silane dendrimers are immobilized by covalent bonding.⁴⁰

Curable organosiloxane coating has been invented for the production of coated fabrics.⁴¹ It is crosslinked by addition of Si-bound hydrogen onto aliphatic multiple bonds (e.g., α,ω -vinyl dimethylsiloxyl-terminated polydimethylsiloxane) and organic acids which have boiling points above 100°C.⁴¹ Acids used do not inhibit the hydrosilylation catalyst and provide reduced odor in the silicone rubber formulation.⁴¹ Examples of such acids include undecenoic, ethylhexanoic, oleic, stearic, malic, and citric acids.⁴¹

9.9 COMPOSITES

Natural fiber reinforced plastics, besides having advantages compared to glass- and carbon reinforced materials (mechanical properties/weight, CO₂-equilibrium), also have properties that limit their application possibilities.⁴² Emissions and unpleasant odors at certain temperature and humidity conditions are of concern.⁴²

It was found that microcellular composites have low odor concentration.⁴³ Chemical foaming agents on their decomposition produce gas, which partially escapes from micro-composite carrying with its odorous substances.⁴³ It was also found in this paper that extruded composites had more intensive odor than injection molded composites of the same composition because the residence time in extrusion was longer, which affected decomposition of the material.⁴³

A disadvantage of the use of natural fibers in the reinforcement of polypropylene is their poor thermal stability, which results in their degradation at processing temperatures of the composites.⁴⁴ This leads to the formation of low molecular weight compounds that are responsible for undesirable odors.⁴⁴ The following volatile substances have been detected by GC/MS: benzenic and phenolic compounds (2,4-bis(1,1-dimethylethyl)phenol, 1-methyl-4-(1-methylethylidene) cyclohexene, 1-methyl-2-(1-methylethyl)benzene, benzoic acid, methyl ester of benzoic acid, 1-methyl-4-(1-methylethyl)-1,3-cyclohexadiene, p-tert-butylphenol, 1,3-diethylbenzene, 2,6-bis(1,1-dimethylethyl)-2,5-cyclohexadiene-1,4-dione, and phenol), aliphatic compounds (pentadecane, heptadecane, hexadecane, 2,6,10,14-tetramethyl pentadecane, and squalane), alcohols (furanmethanol and 1-tetradecanol), carboxylic acids and derivative (hexadecanoic acid, dodecanoic acid, and methyl ester 9-octadecenoic acid) and other compounds (eugenol, vanillin, isopropyl palmitate, and diethylstilbestrol).⁴⁴

A composite has been patented which can remove moisture, liquids, and odors and has antimicrobial capabilities.⁴⁵ The composite can be used to line an outer and inner functional surfaces, such as shelf, drawer, cabinet, or refrigerator, or as a backing for other surfaces, such as carpeting, fabric, upholstery, drapes, and the like.⁴⁵ Odor absorption agents include sodium bicarbonate, activated carbon, zeolites, ion exchange media, activated alumina, and silicates.⁴⁵

Composite material for odor control from wastes, e.g., daily cover for landfills and composting applications, was developed.⁴⁶ The composite material includes fiber web and a zeolite containing metals to promote absorption of gasses.⁴⁶ Metals involved include K, Li, Mg, Ba, and Fe.⁴⁶ Concentration of zeolite is in the range of 0.4 to 4 wt%. Typical zeolite for this application is clinoptilolite.⁴⁶

Bio-odor generated during the process of making bioplastic composites is controlled by addition of an odor controlling agent.⁴⁷ The formation of odor in bioplastics is caused by natural decay, oxidation, and processing.⁴⁷ Another odor-controlling method includes the addition of fragrances.⁴⁷ The fragrances and odor neutralizers work by altering the chemistry of odorous composition in such a manner that the receptor cells do not recognize the molecule of malodor.⁴⁷

The purpose of this invention is to reduce the odor of composite resin particles.⁴⁸ The particles of the invention contain polyolefin-based resin or polystyrene and are used for the production of expanded articles.⁴⁸ The odor is removed by fluidizing particles at a temperature close to the softening point.⁴⁸ In this process, particles are also pre-expanded.³⁸ The odor of isovaleric acid is diluted in the process 100,000 times.⁴⁸

More than 140 compounds were present in the raw materials and wood plastic composites.⁴⁹ Some compounds were considered wood plastic composites markers such as furfural, 2-methoxyphenol, N-methylphthalimide and 2,4-di-tert-butylphenol.⁴⁹ Hexanoic acid, acetic acid, 2-methoxyphenol, acetylfuran, diacetyl, and aldehydes were the most important odorants.⁴⁹

9.10 COSMETICS

Improvement of the odor of various components of cosmetics formulations is one of the major goals in this field. Solvents derived from petroleum have relatively low odor, but practically odorless solvents can be obtained from paraffinic stock (e.g., alkylate type isoparaffinic solvents).⁵⁰ This makes them suitable for application in cosmetics.⁵⁰ White oils are suitable because of their low odor but have too high a viscosity for cosmetic purposes.⁵⁰ Isoparaffinic solvents produced from alkylate fraction were percolated over a variety of adsorbents (4A molecular sieve, charcoal, silica gel, activated alumina, activated charcoal, 13X molecular sieve, and their combinations) at room temperature.⁵⁰ Cosmetic grade, very low odor solvents were obtained from the following combinations: 1/3 activated alumina + 1/3 13X molecular sieve + 1/3 activated charcoal or 1/2 activated alumina + 1/2 13X molecular sieve.⁵⁰

Reduced odor esters, such as benzoate, octoate, glycol dibenzoate, and aliphatic emollient esters are subject of this invention.⁵¹ The improved process comprises removal of catalyst from crude ester after the esterification reaction is complete, before neutralization.⁵¹ This improves their odor, and they become suitable for cosmetics, pharmaceutical and medical purposes.⁵¹

Cosmetic composition, which contains surfactant, having oxyethylene group in the molecule, and tert-butanol, has stable odor properties.⁵² Normally addition of surfactant causes odor generation with time.⁵² Addition of tert-butanol (0.02 wt% of 0.1% aqueous solution) eliminates the problem.⁵²

Natural pearlescent pigment derived from fish is deodorized by contacting it with complex metal hydride.⁵³ Addition of a weak acid subsequent to treatment with complex metal hydride enhances the deodorization process.⁵³ Pearlescent pigments are used in toiletries, such as shampoos, hair rinses, lotions, creams, soaps, cosmetics to improve their attractiveness.⁵³ Guanine contains amines which cause deterioration and provide unpleasant odor to pearlescent pigment.⁵³ This odor is present even after several bleaching and washing steps.⁵³ The invention contains detailed description of deodorization beginning

from separation of guanine crystal from fish.⁵³ Sodium borohydride is a preferred complex hydride used in the process.⁵³ The weak acids useful in this patent are formic, acetic, citric, malic and other acids, with acetic acid being preferred.⁵³

There is a skin treatment composition comprising antibacterial zeolite and trisalt ethylenediaminehydroxyethyl triacetate.⁵⁴ This composition is useful as a deodorizing skin treatment composition, deodorizing cosmetics, antiperspirant cosmetics, and odor eliminating cosmetics.⁵⁴

Cosmetic composition containing hydroxyethers is used as oil body in cosmetic and pharmaceutical preparations.⁵⁵ Other components of deodorants include active ingredients, such as antimicrobial agent, enzyme inhibitor, odor absorber, and odor masking agent.⁵⁵ Trialkyl citrates, such as trimethyl citrate, tripropyl citrate, triethyl citrate, and tributyl citrate are esterase inhibitors and they reduce formation of odor.⁵⁵ Suitable odor absorbers are substances which are able to absorb and retain odor-forming compounds.⁵⁵ The odor-masking substances are fragrances or perfume oils.⁵⁵

A method of refining ultraviolet absorber used in cosmetics has been proposed.⁵⁶ In this process UV absorber is brought into contact with absorbent.⁵⁶ This process is applicable to UV absorbers in which aldehydes are causative substances of odor.⁵⁶ UV absorbers used in cosmetics include derivatives of cinnamic acid, benzophenone, p-aminobenzoic acid, or salicylic acid.⁵⁶ They are poor in long-term stability.⁵⁶ They can be oxidized and deteriorate with time giving color and odor.⁵⁶ Adsorbents used in this invention include silica gel, activated clay, and active alumina/magnesia hydrate.⁵⁶

A cosmetic preparation that contains L-ascorbic acid 2-phosphate sodium salt having long-term stability is patented.⁵⁷ L-ascorbic acid 2-phosphate sodium salt decomposes causing yellowing and strange odor formation, especially when stored at temperature of 30°C or higher.⁵⁷ Addition of arginine, urea, and/or triethanolamine prevents decomposition.⁵⁷

A combination of octyl salicylate and 1,3-dihydroxyacetone has been patented for cosmetic preparations.⁵⁸ 1,3-Dihydroxyacetone disintegrates over time because of its oxidation, especially in aqueous cosmetics.⁵⁸ The decomposition products of 1,3-dihydroxyacetone include hydroxymethylglyoxal, formaldehyde, glycolic acid, formic acid, acetic acid, and pyruvic acid.⁵⁸ These degradation products give unpleasant odor to cosmetic formulations.⁵⁸ It known that octyl salicylate suppresses perception of odor of these decomposition products.⁵⁸

A process of removing odors from hydrocarbons is disclosed.⁵⁹ Odor-free hydrocarbons so obtained are particularly suitable for cosmetic applications.⁵⁹ The process includes contacting hydrocarbon phase with aqueous alkaline phase, mixing them together, and separating them.⁵⁹

Sterilization of polypropylene packaging for cosmetics by γ -irradiation causes formation of 38 odorants which have been identified by GC/MS and the odorants were assigned to different types of odors determined by olfactometry.⁶⁰

A method of reducing odor of 1,3-butylene glycol includes contacting the 1,3-butylene glycol with an activated carbon selected from wood-based activated carbons and chemically activated carbons.⁶¹

9.11 DEFENCE MATERIALS

Defence and security industries use electronic noses for detecting land mines.⁶² Nitroaromatics are sampled by polymers which have high sensitivity and relatively narrow specificity for nitroamines.⁶³ The device can identify odors at multiple concentrations without explicit training.⁶³ The device showed 100% detection and no false alarms for the land-mine-related compound dinitrotoluene at concentrations as low as 500 pp-trillion.⁶³ In calibration tests, signals from buried anti-personnel land mines were clearly discriminated from background.⁶³

Stable samples of peroxidic explosives odor were patented.⁶⁴ The method uses neutral ionic liquids to stabilize peroxide explosives and produce their stable solutions.⁶⁴ This stable odor sample is needed for test measurements, to calibrate detectors, and to train explosives sniffer dogs or other biological detection techniques.⁶⁴ Device and methods were developed for the impregnation of air with the vapor or aerosol of a substance in a controllable manner to enable the testing or training of detection means to evaluate and quantify the presence of the substance in an enclosed volume in a real environment, and in particular to enable production of training aids for dogs to detect explosives and narcotics.⁶⁵

9.12 DENTAL MATERIALS

Dental composition and methods of use are provided in a patent.⁶⁶ The composition comprises multifunctional acrylate compounds, initiator, and alcohol.⁶⁶ Storage odor is detected after storing for a significant period of time.⁶⁶ One frequently-used composition, Extoral, is a visible-light-cured dental resin formulation which has strong odor caused by methyl methacrylate.⁶⁶ When ethanol or other alcohols are used as a solvent, the presence of storage odor is minimized.⁶⁶

Odor-detecting toothbrushes have been designed.⁶⁷ The odor detection system is integrated into the toothbrush and comprises a gas sensor indicator.⁶⁷ Bad breath can be detected by the gas sensor indicator.⁶⁷ Sulfur-based compounds, such as hydrogen sulfide, methyl mercaptan, and dimethyl sulfide are detected.⁶⁷

9.13 ELECTRONICS

In this section we reflect on growing interest in the development of electronic devices for odor-sensing and generation.⁶⁸ Electronic odor sensor is configured to correlate the received output signals related to the presence or absence of an odor.⁶⁸ Amplifiers have semiconductor layers configured to produce output signals responsive to conductivities of their organic semiconductor layers.⁶⁸ The process of detecting odor includes its absorption into organic semiconductor layers and measurement of signal produced by an array of amplifiers in response to the act of absorbing.⁶⁸ The process also includes determination of the identity of the absorbed odor based on the measured set of output signals.⁶⁸

An electronic device with an aromatic odor generating unit is composed of a body, aromatic odor generating unit, and a fan.⁶⁹ The aromatic odor generated by the aromatic odor generating unit is channeled from the body to the electronic device by the air flow produced by the fan, so as to achieve an improved operation environment.⁶⁹ A negative

ion generating unit can mix odors with negative ions to provide functions for invigorating people's spirit.⁶⁹

A portable apparatus for recognizing and storage of taste and odor has been developed.⁷⁰ The apparatus is comprised of a sensor for recognizing taste/odor information, modulator of information to change it to electrical signal, a recording unit to convert signal information into a standardized format, a storage unit to store information in memory, an input/output interface for transmitting the stored taste/odor information to THE outside, and the power source to supply power to all these units.⁷⁰

Another apparatus can reduce the amount of water in the sample before contacting the sample with a sensor.⁷¹ Loss of sensitivity of most sensors is caused by water presence.⁷¹ Most likely water molecules form hydroxyl groups on the oxide surface which alter the response of sensors by reducing their sensitivity.⁷¹ The sensor has a membrane which is capable of reducing the amount of water present in the sample because the membrane is partially permeable to water but impermeable to odorous substances.⁷¹

A digital odor generator has a housing and a cylindrically-shaped odor chamber with a plurality of separate odor compartments.⁷² A porous hollow cylinder with odorant is located in each odor compartment.⁷² The nozzle has openings equal to the number of compartments.⁷² It allows the user to select and smell an odor coming from a singular compartment.⁷²

An apparatus and method of assessing odor have been patented.^{73,75} The apparatus comprises electronic nose, neural network for mapping odor structure, pre-learned axis of odor pleasantness, and output for sending information about odor and its assessment regarding odor quality.^{73,75}

The challenges and benefits of fabricating gas sensors using complementary metal oxide semiconductor technology and the integration of associated circuitry onto a single silicon chip have been discussed in a book chapter.⁷⁴

The odor absorbent layer comprises polyvinylidenechloride and magnesium oxide, magnesium salt, magnesium hydroxide, zeolite, or they combinations.⁷⁶ The use of the film in ostomy pouches and other medical products is discussed.⁷⁶

System and methods for a mobile electronic system that gathers and analyzes odors, airborne chemicals and compounds.⁷⁷ Representation of the odors, airborne chemicals and/or compounds can be generated.⁷⁷ A model can be generated based on the representation data. The model can be searched for candidate matches, solutions, or other results.⁷⁷

9.14 FIBERS

Accelerated hydrothermal degradation of fibers of *Phormium tenax* (New Zealand flax) has been studied by GC/MS. Acetic acid and furfural are emitted from the fibers during their degradation.⁷⁸ Accelerated hydrothermal ageing of fibres for 55 days at 70°C resulted in the production of acetic acid at a level greater or equal to 1.65 mg g⁻¹ fiber.⁷⁸ This corresponds to 8.5% of the acetyl groups present in the fiber.⁷⁸ The acetic acid evolved can damage the fiber. In addition, a series of short to medium chain aliphatic aldehydes that were derived from the oxidation of long chain unsaturated fatty acids in the fibers and a small group of products that were derived from carotenoids were also emitted.⁷⁸

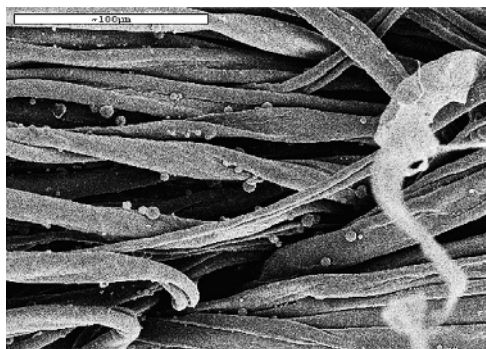


Figure 9.3. SEM micrograph of cotton fabric impregnated with microcapsules. [Adapted, by permission, from Monllor P, Bonet M A, Cases F, *Eur. Polym. J.*, 43, 2481-90, 2007.]

Flavor microcapsules were tested on cotton fabrics.⁷⁹ Microcapsules were produced using encapsulated nanoparticles. The composition of the wall determines the release rate of encapsulated product (e.g., fragrance).⁷⁹ Impregnation was found to be the most efficient method of application of microcapsules onto the cotton fabric.⁷⁹ Figure 9.3 shows microcapsules attached to the surface of cotton fibers after impregnation.⁷⁹ Some odor intensity remained after washing cycles and the rubbing test.⁷⁹

A variety of volatile compounds, including sulfur-containing compounds, were emitted from wool with their concentration increasing with temperature and

humidity in most cases.⁸⁰ The following substances were detected by GC/MS studies: ethanol, acetone, 2-methylpentane, 2-butanone, 3-methyl pentane, hexane, methylcyclopentane, 1,1,1-trichloroethane, 1-pentanol, toluene, hexanal, heptanal, 2-octanone, nonane, octane, decane, hydrogen sulfide, methanethiol, COS, CS₂, dimethyldisulfide, dimethyltrisulfide, and DMSO.⁸⁰ Degradation of wool and particularly wool grease is thought to be responsible for the occurrence of the detected compounds.⁸⁰ When antioxidant was incorporated into the wool scouring process, it resulted in a reduction of the number of head-space volatile compounds detected, and a distinct improvement in the pleasantness of the odor with an accompanying reduction of its intensity.⁸⁰

The isotherms of chloroform and iron ion adsorption onto activated carbon fibers in a single solution (chloroform or iron ion) and in a binary mixture solution (chloroform and iron ion) were investigated to estimate the competitiveness between chloroform and iron ions.⁸¹ The amount of adsorbed iron ions increased with increasing pore volume of the activated carbon fibers, while that of chloroform decreased.⁸¹ The amount of chloroform adsorbed onto the activated carbon fibers in the binary mixture solution was greater than that in the single solution.⁸¹ These results indicate that the adsorption of chloroform and iron ion onto activated carbon fibers could be competitive.⁸¹

Liquid deodorant was invented for deodorization of fibers and hair cosmetics.⁸² Organic dibasic acid is used as deodorant. It is selected from organic dibasic acids and/or salts having difference between the first acid group dissociation index and the second acid group dissociation index of 1.7 at 25°C.⁸² The following acids fall into this category: maleic acid, 2-isopropylmalonic acid, 2,4-butylmalenic acid, hexahydrophthalic acid, 5-norbornene-2,3-dicarboxylic acid anhydride, and many others.⁸² The deodorant of the present invention is effective for tobacco, sweat, pet, and cooking odor.⁸²

Fibrous materials include a plurality of natural fibers treated with a carboxylic acid-based odor control agent.⁸³ The acid-based control agent is bound to fibers by an organo-silicone polymer binder.⁸³ The binder is porous, so as to expose the odor control agent to ammonia and other odoriferous gases.⁸³ The acid-based control agent is made out of multi-carboxylic acid-modified chitin or chitosan.⁸³

Odor eliminating fiber has an odor indicator.⁸⁴ Fiber discolours through absorption of a smelling gas.⁸⁴ Applications include refrigerators, trash cans, kitchen cabinets, shoe cupboards, and the like.⁸⁴ The odor eliminating fibers contain metal or metallic compounds discoloring through absorption of smelling gas.⁸⁴ The metals or their compounds are selected from silver, copper, and their metallic compounds, which discolor to black with sharp color change on absorption of a sulfur-containing gas.⁸⁴

Fiber for elimination of human-based odors and repelling insects contains an odor absorbent and insect repellent.⁸⁵ The insect repellent is N,N-diethyl-meta-toluamide, but other insect repellents, such as citronella oil, eucalyptus oil, lavender oil, and others, may also be used.⁸⁵ Odor absorbent is carbon or its mixture with silver.⁸⁵

Cellulosic fiber with odor-control characteristics contain biocide and enzyme, urease inhibitor.⁸⁶ The active components are applied by impregnation. Liquid carriers include triacetin, propylene carbonate, polyethylene glycol, and many others as long as they do not affect wettability of cellulosic fibers.⁸⁶ Fatty acid amides (e.g., Catavlon) are used as odor-inhibiting agents.⁸⁶ Preferred biocides include salicylic acid-N-octyl amide, triclosan, 4-chloro-3,5-dimethyl phenol, tetracycline, and 3,4,4'-trichloroanilide.⁸⁶ The same cellulosic fiber can be used in a sheet form, production of which is described elsewhere.⁸⁷

Adsorbent articles such as diapers, feminine hygiene products, or training pants, contain an odor control article having positive charge.⁸⁸ The chemical compound useful in this patent can be aluminum chlorohydrate, which is capable of immobilizing bacteria that cause odor.⁸⁸ The immobilized bacteria cannot multiply and therefore they cannot produce odorous substances.⁸⁸

Cellulosic fiber composition having odor control contains activated urease inhibitors.⁸⁹ Ureases are proteins produced by microorganisms to break down or modify urea.⁸⁹ Urease inhibitors include inorganic and organic compounds, such as boron compounds, fluorides and sulfur compounds, hexamethylenetetramine, dithiocarbamates, thiuram disulfides, sulfides, phenyl phosphorodiamidate, polyhexamethylene biguanidine, n-butyl thiophosphoric triamine, and a large number of other organic compounds.⁸⁹

Twenty-four compounds were identified in the volatile fraction of flax fibers with a high occurrence of aliphatic aldehydes, phenols, and furans.⁹⁰ The results point to a critical temperature between 215 and 230°C at which the odor of flax fibers becomes more intense, more complex, and with unpleasant features.⁹⁰

Mixtures contain reaction products of one or more amines with one or more epoxides and additionally, isocyanates.⁹¹ Application of these mixtures to textiles, especially polyester fiber fabrics, reduces unpleasant sweaty odor after physical exercise.⁹¹ The effects are very durable to laundering.⁹¹

9.15 FILMS

Control of permeation of organic compounds that impart flavor and odor is one of the major functions of film packaging. Films protect the package contents from either the absorption of unwanted odors or the loss of volatile flavoring ingredients. Important flavor consideration is related to "flavor scalping". It is a selective absorption of certain flavor constituents from the product. Polyolefins are known flavor scalpers. Cellophane, saran, and polyvinylchloride have good barrier properties. Cellulose acetate and polyethylene are poor odor and flavor barriers.

Changes in odor and taste related to food packaging can be traced to degradation of the packaging materials during processing.⁹² The degradation of polyethylene in a commercial extrusion coating process was studied by analyzing degradation products present in smoke sampled at the extruder die orifice.⁹² Two low-density polyethylenes with similar melt flow indexes and densities, but obtained from different producers, were investigated.⁹² A third polymer contained recycled material.⁹² More than 40 aliphatic aldehydes and ketones, together with 14 different carboxylic acids, were identified in the smoke (for their composition consult Section 8.19, Table 8.1).⁹² Increase in extrusion temperature, in the range 280-325°C, increased the amounts of the oxidized products in the smoke.⁹² Ticker film gave higher amounts of volatiles.⁹² The recycled polymer gave lower concentrations of degradation products.⁹² Differences between the two virgin polymers may be related to differences in the manufacturing process.⁹²

Contamination of food products by organic substances originating from materials in contact was studied by modeling and comparison with results for 38 substances.⁹³ Pair contact energies were calculated at atomistic scale with an *ab-initio* forcefield.⁹³ The choice of an appropriate food simulant is of significant concern to assess the migration of plastics additives into food.⁹³ Results demonstrated that the chemical affinity of plastic additive or polymer residue for a given liquid involves a relationship with the relative size of the solute, its flexibility, and its polarity.⁹³

Multiple headspace solid-phase microextraction followed by gas chromatography-mass spectrometry analysis was used to determine the main volatile radiolysis products formed by γ -irradiation of flexible multilayer food packaging samples.⁹⁴ In γ -irradiated material, 29 compounds were identified (17 of which were absent in the non-irradiated samples).⁹⁴ The main volatile radiolysis products were: 1,3-di-*tert*-butylbenzene, 2,6-di-*tert*-butyl-1,4-benzoquinone, 4-*tert*-butyl-phenol, butanoic acid and valeric acid.⁹⁴

The scalping of aroma compounds may affect the sensory properties of wines packaged in plastics by reducing the intensity and changing the character of the original aroma.⁹⁵ Ethyloctanoate was sorbed more into polypropylene than into low density polyethylene and at much higher extent than linalool because of differences in polarity of the molecules.⁹⁵ This difference in sorption caused an imbalance of the original aroma composition. Ideal Fickian transport diffusional character was confirmed.⁹⁵

Shredded cabbage was packaged in three packaging types: bags of monooriented polypropylene film, polyethylene trays overwrapped with a multilayer polyolefin, and plasticized PVC film.⁹⁶ All types of packaging effectively controlled the weight loss.⁹⁶ Polypropylene packaging was significantly better in general appearance, wilting, and browning but developed an off-odor.⁹⁶ No off-odor was detected in samples packaged in PVC and PP.⁹⁶

An antioxidative plastic film coated with microcapsules containing volatile horseradish extract was developed.⁹⁷ The amount of extract released from the film can be modulated by the chitosan content of the microspheres.⁹⁷ A horseradish-coated film efficiently enhanced the stability of both pork and fish.⁹⁷

Odor-resistant, film-forming composition is a barrier to odor migration into its contents.⁹⁸ It contains silicon compound with an amine group and a plurality of hydrolyzable groups.⁹⁸

Wrap film for food application is produced from crosslinked, laminated polyethylene.⁹⁹ It has low odor properties.⁹⁹ Fatty acid esters used as an additive for easier film production may produce pungent odor if they have less than 6 carbon atoms.⁹⁹ Use of stearic acid and oleic acid esters lowers odor emission.⁹⁹

Articles for reduction of atmospheric odors are described in an invention.¹⁰⁰ They contain a thermoplastic polymer, odor-reducing agent, and fragrance.¹⁰⁰ Odor-reducing agents can be inorganic compounds (zinc oxide, aluminum oxide, zeolite, silica gel, active carbon, and many others), hydrazines, cyclodextrin, organic polymers, and their mixtures.¹⁰⁰ Odor-reducing agents absorb odorous substances or interact with them by ionic, electrostatic, dipole-dipole interaction.¹⁰⁰

The plastic film contains odor barrier and fragrance.¹⁰¹ Polyethylene or polypropylene film contain fragrance and bis-fatty acid amide, which imparts sufficient impermeability to odors.¹⁰¹

Odor transmission-resistant film has been patented.¹⁰² The film contains polyethylene layer (moisture barrier) on both sides of a barrier layer from polyamide manufactured by coextrusion.¹⁰² Odor reduction was found significantly enhanced when the odiferous material was in contact with a moisture barrier (polyethylene), which, in turn, was in contact with the odor barrier.¹⁰² Polyethylene layer contained fragrance.¹⁰²

Film or laminate comprising ethylene-based resin has low odor property.¹⁰³ It is obtained from an α -olefin having 4 to 10 carbon atoms.¹⁰³ Resin has controlled melt flow rate, density, rheological properties, and a number of methyl branches.¹⁰³ The resin used in this application can be processed at low temperature, therefore, it has a low emission of odorous substances.¹⁰³

Film material having antimicrobial and/or odor coating is a polyolefin-based film, coated on one side with water resolvable resin containing skin.¹⁰⁴ The coating contains antimicrobial and/or odor absorbing agents susceptible of being activated by organic liquids and blood liquids. It is designed for disposable sanitary articles.¹⁰⁴ Odor absorbing coating is designed to absorb objectionable odor molecules, such as sulfides, amines, fatty acids, and ammonia.¹⁰⁴

The propylene-based polymer is used for the production of film and articles with good taste and odor performance.¹⁰⁵ In the packaging industry, ozone is commonly used for sterilization of drinking water.¹⁰⁵ During the bottling process, ozone is applied as the last step to disinfect and kill any air-borne microorganisms.¹⁰⁵ Due to its strong oxidizing action, ozone can kill bacteria, but it also causes undesirable reactions which are the source of off-taste odor that characterizes ozonated water, especially if packaged in flexible polyethylene containers.¹⁰⁵ The patent analyzes all the aspects of production of polypropylene film specially designed for ozonated water.¹⁰⁵

An odor containment system for use with flexible bags has been patented.¹⁰⁶ It is used for storing or transporting products or materials that may produce undesirable odors.¹⁰⁶ The system uses a flexible bag, which is configured to produce odor-masking scent, absorb odors, and neutralize odors.¹⁰⁶

9.16 FLOORING

2-Ethyl-1-hexanol is detected in indoor air at relatively high concentrations.³⁵ The emission mechanism for 2-ethyl-1-hexanol has been explained (see Figure 9.2).³⁵

Heptanal, octanal, nonanal, decanal, 2-decenal are products of degradation of oleic acid which is used in linoleum, eco-lacquers, nitrocellulose lacquers, and alkyd resin.¹⁰⁷ Carpets are degraded indoors by ozone, producing aldehydes and other unidentified VOC components.¹⁰⁷ An emissions trap (an adsorption cloth attached to the PVC flooring) improved the indoor air quality of a school building with elevated air concentrations of 2-ethyl-1-hexanol.¹³ The performance of the device is not affected by differences in RH (35–85%), temperature (30–40°C), and by accelerated aging simulating up to 10 years product lifetime.¹³

A liquid composition for removal of odors from carpets includes an antimicrobial agent, an enzyme inhibitor, and odor-reacting compound.^{108,109,112} The composition has been effective in the neutralization of odors associated with decomposition of organic materials (e.g., urine or food spills) by absorbing and removing the odor-generating source.¹⁰⁸ Some antimicrobial agents (e.g., 2-bromo-2-nitro-1,3-propanediol) also act as enzyme inhibitors.¹⁰⁸ Some odor-absorbing compounds, such as zinc ricinoleate, act as enzyme inhibitors.¹⁰⁸ Other antimicrobial agents useful in this application include silver zirconium phosphate, zinc oxide, imidazoylidinyl urea, cationic quaternary ammonium salt, sodium sorbate, potassium sorbate, sorbic acid, grapefruit seed extract, and many other.¹⁰⁸ Preferred antimicrobial agents are N,N'-dimethylol-5,5-dimethyl hydantoin or N-methylol-5,5-dimethylhydantoin.¹⁰⁸ Enzyme inhibitors, such as urease inhibitors, control ammonia generation.¹⁰⁸ They include salts of zinc, copper, zirconium, aluminum, silver, and tin.¹⁰⁸ Also, some organic compounds, such as hydroxybenzyl aldehyde and quaternary ammonium compounds are useful as enzyme inhibitors.¹⁰⁸ Odor-reacting compounds include benzyl aldehyde, formaldehyde, p-hydroxybenzaldehyde, octanal, salicylaldehyde, and many others such as ketones reacting with amines or oxidizing agents.¹⁰⁸ Odor absorbing compounds can also be included.¹⁰⁸

A composition which imparts odor resistance contains polyester, wax-modified polymer, and zeolite.¹¹⁰ Wax and polymer are covalently attached to one another. Wax-modified polymer facilitates polyester in binding zeolite.¹¹⁰ Wax can be natural or synthetic product and polymer can be melamine resin, phenolic acid resin, or urea resin.¹¹⁰ There is a commercial product (Cerol-EX) which is a reaction product of paraffin and melamine resin. The zeolite can mask, neutralize, absorb, and reduce odors.¹¹⁰

High odor eliminating property is provided to a building material for interiors by compounding a hydrazine. VOC is captured by the product of this invention if VOC is generated from a formaldehyde-based adhesive. Hydrazine and organic carbide are compounded into building material to capture odorous substances including aldehydes.

9.17 FOAM

Isocyanatocyclohexane and isothiocyanatocyclohexane are found in urban and industrial air.¹¹⁴ They are used in the automobile industry and building insulation, as well as in the manufacture of foams.¹¹⁴ The concentrations ranged between 246 and 29 $\mu\text{g m}^{-3}$ for isocyanatocyclohexane and isothiocyanatocyclohexane, respectively, in industrial areas.¹¹⁴

Urban and residential locations had concentrations ranging between 164 and 29 $\mu\text{g m}^{-3}$ for isocyanatocyclohexane and isothiocyanatocyclohexane, respectively.¹¹⁴

Low odor flexible polyurethane foams are prepared.¹¹⁵ Ethylene oxide-rich polyethers did not produce low odor foams.¹¹⁵ If these foams contain urethane, urea and isocyanurate groups, they have improved odor.¹¹⁵

Metal salts of ricinoleic acid are used in the production of polyurethane foams.¹¹⁶ This is in relationship to efforts by the automotive industry to reduce the odor of foams.¹¹⁶ Adding metal salts of ricinoleic acid permits production of polyurethane foams which have lower emission values, better flame retardancy, and less odor.¹¹⁶

Amine catalyst composition of this invention permits production of low odor foams.¹¹⁷ The catalyst used in this patent is 3-(bis-(dimethylaminopropyl)-propionamide.¹¹⁷ In addition to low odor, foams have also low VOC emission.¹¹⁷

Odorless polyurethane foams are produced from odorless polyols.¹¹⁸ The polyester polyols are manufactured using a stripping step to remove odorous volatile compounds.¹¹⁸ Odors in polyurethane foams come from non-reactive impurities that are present in polyisocyanate, polyol, water, and other ingredients.¹¹⁸ Volatile amine catalysts can contribute to the odor of foam.¹¹⁸ Blowing agents are highly volatile and they can contribute to the foam odor. Polyols are manufactured at high temperatures (260°C) for up to 48 hours.¹¹⁸ Under these conditions, it is possible that impurities are formed.¹¹⁸ Some polyols have a distinct sweet odor.¹¹⁸

Odor free foam for mattresses is produced by dissolving cyclodextrin in water to form a solution, adding this solution to a reacting mixture of polyol and isocyanate to produce odor-free or reduced odor foam.¹¹⁹ Certain cyclodextrins have a “snow cone cup-like” molecular shape, which allows molecules to bind with odorous substances so they are not any longer detected as the scent.¹¹⁹

A flame resistant flexible polyurethane foam can be produced with reduced odor for under-the-hood vehicle applications, which require sound deadening and vibration management.¹²⁰ The odor suppressants can be selected from the group consisting of cupric oxide, cupric acetate, cuprous acetate, copper metal, complexes of cupric cation or cuprous cation and ligands containing one or more nitrogen atoms.¹²⁰

An odor-absorbing foam composition comprising a cyclodextrin crosslinked with a polyurethane prepolymer is applicable to a personal care product or wound care.¹²¹

A rubber foam composition has low metal corrosive properties, low fogging properties, and reduced odor.¹²² The α,α' -di(t-butylperoxy)diisopropylbenzene is an organic peroxide which produces a reduced odor.¹²²

The vegetable-based polyol was used which has an odor rating lower or equal to 2.7 according to the Society of Automotive Engineers SAE J1351 odor test.¹²³ The foam produced from low odor polyol was encapsulated in an odor barrier fabricated from polyethylene.¹²³

9.18 FOOD

Food may be affected by packaging in a few ways: odorous substances can be transferred from packaging material to food product, packaging does not provide food with sufficient protection from action of external elements and food material generates foreign odors, process of production causes formation of odorous substances which are formed or transferred to foods, or packaging material absorbs some food flavors, causing changes in the balance of flavors (see Section 9.15). These aspects of food odors are discussed below.

Food and beverage products stored in polyethylene containers may absorb some of the volatile components present in polyethylene and become tainted by a characteristic “plastic” odor.¹²⁴ 8-Nonenal was found to be the major contributor of “plastic” odor in corn chips.¹²⁴ The concentration of 8-nonenal in polyethylene increases with increase in temperature of its processing, the temperature of storage, and the addition of recycled polyethylene. Use of antioxidant in the process mixture reduces the formation of 8-nonenal.¹²⁴

Cyclodextrins and their derivatives are used to suppress unpleasant tastes and odors or to achieve a controlled release of certain food constituents.¹²⁵ The soluble cyclodextrin polymers interacted with bitter flavonoids of citrus fruits (naringin and limonin) performing function of bitter taste-masking agents.¹²⁵

More than 600 compounds from the volatile fraction of dry-cured ham were identified.¹²⁶ They covered a wide variety of structures and chemical functions.¹²⁶ Only 29 of them proved to be odor-active.¹²⁶

Four rice samples of the long-grain type were tested using an electronic nose.¹²⁷ The electronic nose was able to differentiate between varieties of rice.¹²⁷

A commercial electronic nose (Cyranose 320TM) was used to analyze ethanol and acetic acid generated from spoiled beef.¹³⁵ Because of non-selective nature of sensors, simultaneous use of multiple sensors provides better classification accuracy for discriminating various gas concentrations as compared to using individual sensors.¹³⁵

Four optical fiber sensors have been used to distinguish odors of different drinks.¹³⁶ The system was trained to distinguish between grape juice, wine, and vinegar.¹³⁶ The sensors can be located 6 km away from their optical header.¹³⁶

The (E)-3-unsaturated volatile acids, alcohols, and aldehydes are commonly found as odorants or pheromones in foods, playing a vital role in the attractiveness of foods.¹³⁴ Among (E)-3-alkenoic acids the odor quality changed from sweaty *via* plastic-like to sweaty and waxy.¹³⁴ Among (E)-3-alken-1-ols and (E)-3-alkenals, the odor quality changed from grassy, green to an overall citrus-like, fresh, soapy, and coriander-like odor with increasing chain length.¹³⁴

An antioxidative plastic film coated with microcapsules containing volatile horseradish extract was developed.⁹⁷ The presence of naturally occurring antioxidants in the extract was confirmed by high-performance liquid chromatography.⁹⁷ Covering pork and fish fillets with the antioxidative film delayed oxidative discoloration and rancidization.⁹⁷

Active and intelligent packaging is based on a deliberate interaction of the packaging with the food and/or its direct environment to improve food quality and safety.¹²⁸ Such technology includes advances in delayed oxidation and controlled respiration rate, microbial growth, and moisture migration.¹²⁸ Other examples are carbon dioxide absorbers/emitters, odor absorbers, ethylene removers and aroma emitters, while intelligent packag-

ing includes time-temperature indicators, ripeness indicators, biosensors and radio frequency identification.¹²⁸

Chemical and sensory changes in pasteurized milk stored under fluorescent light in bottles made of multilayer pigmented HDPE+TiO₂+carbon black, monolayer pigmented HDPE+TiO₂, clear polyethylene terephthalate, and pigmented PET+TiO₂ were monitored for a period of 7 days.¹²⁹ Milk packaged in coated paperboard cartons and stored under the same experimental conditions served as the control sample.¹²⁹ Good protection of milk packaged in all packaging materials was achieved with regard to microbiological and chemical parameters.¹²⁹ The best overall protection for the product was provided by the multilayer followed by the monolayer TiO₂-pigmented HDPE bottle.¹²⁹

The influence of packaging polymers (glass, polypropylene or polystyrene) on the sensory and physico-chemical characteristics of yogurts was investigated during 28 days of storage at 4°C.¹³⁰ Glass had the lowest aroma quantity decrease of the three types of packaging.¹³⁰ Polystyrene packaging seemed to be preferable for limiting aroma compound losses and subsequent fruity note intensities, and for avoiding the development of odor and aroma defects.¹³⁰

Cheese was stored for up to 9 weeks under both fluorescent light and in the dark, packaged aerobically and under modified atmosphere packaging.¹³¹ The cheese samples stored under fluorescent light showed a higher degree of lipid oxidation (3–4 times higher for modified atmosphere packaging samples and 20 times higher for aerobically packaged samples).¹³¹ Free fatty acids, esters, aldehydes, ketones, and alcohols were recorded for all treatments, with aerobic packaging and exposure to light giving higher concentrations of volatile compounds.¹³¹

Larger radiation doses increase the probability of changes in the sensorial characteristics of meat (odor of burned meat).¹³² It was concluded that a dose of 3 kGy is adequate, taking into account the microbiological and sensorial aspects.¹³²

The aim of the study was to analyze volatile formation in cinnamon (*Laurus cinnamomum*) samples after γ -irradiation.¹³³ The irradiation decreased volatile compounds by nearly 56% to 89.5% depending on radiation dose (10–25 kGy).¹³³ Cinnamon irradiated with 5 kGy (smallest dose) lost almost 50% of its volatile compounds.¹³³

Baking soda was used to control odor from discarded organic waste.¹³⁷ The baking soda reduced odor concentration by 70%, by reducing volatile acid concentration (ammonia had less effect on odor concentration).¹³⁷ Absorbent pad containing activated carbon was used to reduce confinement odor in food packages.¹³⁸ Mercaptan absorber was proposed to prolong shelf-life of foods such as cabbage, garlic and onions.¹³⁹ It contains a natural zeolite, such as chabazite or clinoptilolite.¹³⁹

9.19 FOOTWEAR

An odor-absorbent layer enabling substantial removal of malodors from a surface or personal article was developed to be used during temporary storage of shoes.¹⁴⁰ The fibrous layer on the surface of the insert contains fragrance.¹⁴⁰ The porous layer, preferably charcoal, is permanently affixed to the fibrous layer.¹⁴⁰

Deodorizer substrate with a porous carrier having monolithic form contains an odor neutralizing composition.¹⁴¹ Deodorizer of this invention has effective deodorizing capability and long shelf life.¹⁴¹ Carrier is made from microporous polyethylene, having pores

in the range of 45-100 μm .¹⁴¹ Undecylenic acid or its derivatives (methyl or ethyl ester) is used as odor neutralizing composition.¹⁴¹ A flavoring agent is also included.¹⁴¹ The shoe deodorizer eliminates 90% of shoe odor.¹⁴¹

A moisture and odor absorbing inserts for sports footwear incorporate regions of fused activated carbon.¹⁴² A desiccant in a form of spheroidal beads is loosely enclosed in a casing.¹⁴² The silica gel (300-650 m^2/g) and activate carbon (400-500 m^2/g) are porous and have a high surface area available for adsorption.¹⁴²

A hygienic footwear cushion contains bamboo charcoal soot.¹⁴³ This cushion provides improved ability to maintain dryness and keeps shoe bacteria- and odor-free.¹⁴³ The cushion is made from the styrene-ethylene-butylene-styrene copolymer.¹⁴³ Soot consists of 0.1 to 1% of the total composition.¹⁴³

Solar photocatalytic inactivation of bacteria contributes to the removal of odors from footwear using photocatalytic textile.¹⁴⁴ The 5 min of UV-A exposure at 0.13 mW/cm^2 is sufficient for inactivation of *Staphylococcus epidermidis*.¹⁴⁴ The photocatalytic textile is made from polyester coated with TiO_2 .¹⁴⁴ Information on textiles used in the military footwear can be found elsewhere.¹⁴⁵

9.20 FRUITS

The quality and extend shelf-life of perishable and soft fruits such as strawberries, raspberries, and blueberries can be improved by developing packaging strategies.¹⁴⁶ A study on the packaging of blueberries in plastic film for short-to-medium term storage was carried out.¹⁴⁶ Four commercially available films were used as packaging materials: two micro-perforated, a non-perforated, and a macro-perforated.¹⁴⁶ The samples were stored at 4°C for 15 days. Non and micro-perforated packaging films gave the best results.¹⁴⁶

The electronic nose was used to determine the effect of repeated impacts on changes in volatile characteristics of fresh blueberries during storage.¹⁴⁷ Repeated impacts caused no skin rupture or leakage after treatment or during storage.¹⁴⁷ Electronic nose sensor array was able to detect increasing dissimilarity among fresh blueberry fruits following mechanical injury.¹⁴⁷

Twenty-five odor-active compounds were found in papaya fruit.¹⁴⁸ Thirty-one odorants were considered as odor-active compounds in banana fruit.¹⁴⁹

9.21 GASKETS

Gaskets made from olefin polymers are useful in sealing food and liquid containers because they do not contribute to taste and/or odor of the packaged product.¹⁵⁰ Gasket contains linear ethylene polymers, having processability similar to highly branched LDPE.¹⁵⁰ Linear LDPE, depending on polymer density, can adversely affect taste and odor.¹⁵⁰

9.22 INKS

Different commercial electronic noses have been used for odor analysis of solvents on printed packages for food products.¹⁵¹ The best results were obtained with Cyranose 320.¹⁵¹

Low-migration and low odor offset printing ink comprises a colophony-modified phenolic resin and water insoluble fatty acid ester of a multivalent alcohol.¹⁵² Changes in odor and flavor of the wrapped goods caused by printing inks were tested according to DIN 10955.¹⁵²

Liquid electrophotographic inks or toners having reduced odors are developed by using antagonistic odor vector compounds for C₁₀, C₁₁, and C₁₂ hydrocarbons.¹⁵³ Each odor produces a specific stimuli or vector each time the same person is exposed to the same odor.¹⁵³ An antagonistic odor vector is defined in practice as a chemical compound or combination of compounds that, in the vapor phase, will reduce or counter olfactory sensations produced by specific materials.¹⁵³ The antagonistic odor vector substances may belong to many classes of chemical materials, including terpenoids, ionones, pentanones, ketones, benzoates, etc.¹⁵³

Odor control substrate that is applied with an activated carbon ink is provided.¹⁵⁴ The odor control substrate may be dried to drive solvent from activated carbon ink.¹⁵⁴

The oily jet ink comprises pigment, a dispersant, and a water-insoluble organic solvent.¹⁵⁵ This ink does not give alcoholic odor from printed paper after image formation.¹⁵⁵ The solvent used in this application is an ester solvent having a number of carbon atoms in the range of 8 to 15 (e.g., butyl myristate or hexyl laurate).¹⁵⁵

The printing ink contains starch and water-soluble acrylic polymer.^{156,158} The ink disclosed in this invention contains a lower amount of amine resulting in less odor and more stable pH.^{156,158}

A deodorizing container that includes a modified nanoparticle ink is used for disposal of adsorbent articles.¹⁵⁷ The container includes an odor control ink that contains a plurality of nanoparticles modified with a transition metal.¹⁵⁷ Nanoparticles are capable of adsorbing malodorous compounds commonly associated with biological fluids.¹⁵⁷ Transitional metal improves odor-reducing properties of nanoparticles, by providing sites for capturing and/or neutralizing malodorous compounds.¹⁵⁷ The following metals can be used in this application: scandium, titanium, vanadium, chromium, manganese, iron, cobalt, nickel, copper, and zinc.¹⁵⁷

Discussion of printing inks and solvents and their effect on food tainting is included in the review publication.¹⁵⁹ Formulations of printing inks can be found elsewhere.¹⁶⁰

9.23 LANDFILLS

Concentrations of ammonia, hydrogen sulfide, and methyl mercaptan are high in the air above landfills in Taiwan.¹⁶¹ Typical emission gases from landfills include CH₄, CO₂, CO, N₂, O₂, H₂, H₂S.¹⁶¹ Typical vapors detected include: alcohols, organic sulfides, halogen-containing compounds, aromatic hydrocarbons, aldehydes, ketones, alkanes, alkenes, cyclic alkanes, cyclic alkenes, esters, and ethers.¹⁶¹ Natural Effective Microorganisms Enzyme, NEME, was sprayed on selected sampling sites to reduce the concentration of NH₃, H₂S and CH₃SH and the number of flies in landfills.¹⁶¹ The measured odor level was

reduced by 68.1–99.4%, depending on landfill.¹⁶¹ The reduction ratio of NH_3 from landfills averaged 72.2% and 61.1%.¹⁶¹ The measured H_2S and CH_3SH concentrations were under 0.03 ppm.¹⁶¹

A study investigated the odor compounds from different areas in a landfill site, which included the municipal solid waste-related area, the leachate-related area, and the sludge-related area.¹⁶² Nine sampling points were placed and 35 types of odorous substances were measured.¹⁶² The main odorous substances were styrene, toluene, xylene, acetone, methanol, n-butanone, n-butylaldehyde, acetic acid, dimethyl sulfide, dimethyl disulfide, and ammonia.¹⁶² The typical odorous substances varied from area to area. For example, in the municipal solid waste-related area, the highest concentrations of oxygenated compounds were observed at the gas extraction wells, while sulfur compounds were rare.¹⁶² Ammonia in the sludge-related area was very abundant.¹⁶²

Alkanes dominated the non-methane organic compounds released from the aerobically pretreated municipal solid waste, while oxygenated compounds were the chief component of the non-methane organic compounds generated from untreated municipal solid waste.¹⁶³ Aerobic pretreatment of municipal solid waste prior to landfilling reduces the organic content of the waste and the intensity of the non-methane organic compounds emissions, and increases the odor threshold, thereby reducing the environmental impact of landfills.¹⁶³

Effluents from a landfill leachate treatment station were treated *via* incineration with methane-rich landfill gas (at 750°C).¹⁶⁴ A list of the key offensive odorants included 23 chemicals.¹⁶⁴ Upon incineration, the concentration levels of most odorants decreased below threshold levels.¹⁶⁴ The incineration method is a highly efficient tool to remove most common odorants (e.g., reduced sulfur species), while it is not so effective for carbonyls and fatty acids.¹⁶⁴

Dispersion of odors strongly depends on local atmospheric dynamics.¹⁶⁵ Toluene was selected as a typical VOC that is representative of the source and has a high emission rate.¹⁶⁵ The two most representative weather types that lead to the majority of complaints were characterized by high-pressure systems with no wind in both winter and summer.¹⁶⁵ The concentration of toluene at the ground surface was combined with the density of the

population in order to calculate a population exposure in winter and summer.¹⁶⁵ Complaints were mainly in the evening in both winter and summer.¹⁶⁵ The complaints were substantially reduced in winter in the morning and in the afternoon.¹⁶⁵

Figure 9.4 shows an instrument, Nasal Ranger, which is used to measure bad smells in the field.¹⁶⁶ The Nasal Ranger permits mixing two streams of air.¹⁶⁶ Ambient air enters through the holes in the front and mixes with



Figure 9.4. Sniffing out a stench. [Adapted, by permission, from Weber C, *New Scientist*, February, p. 21, 2011.]

odor-free air that enters *via* the filters.¹⁶⁶ Twisting the dial changes the ratio of odorous to filtered air, diluting the stench.¹⁶⁶ This helps to find dilution which cannot be detected.¹⁶⁶

Several methods of detection of smell from landfills are used.¹⁶⁷ Chemical analysis helps in identification of key components of odor.¹⁶⁷ Dynamic olfactometry or sniffing team investigation are applicable to the determination of a global odor plume and estimation of an average annoyance zone.¹⁶⁷ The electronic nose can supply a real-time estimation of the annoyance zone.¹⁶⁷

Gas recovery from landfill using aqueous foam has been patented.¹⁶⁸ Hydrogen sulfide concentration in a landfill can be reduced by dispersing a hydrogen sulfide control agent, such as an iron compound, into the landfill.¹⁶⁸ This can be technically done by injecting a foam-containing hydrogen sulfide control agent.¹⁶⁸

The zeolite-containing composite material is useful in odor control in waste management systems.¹⁶⁹ The composite includes a fiber web and a zeolite containing metals to promote absorption of odorous gas.¹⁶⁹ Useful zeolite contains 0.2 to 4 wt% of Zn and 0.4 to 4 wt% of one or more metals chosen from K, Li, Mg, Ba, and Fe.¹⁶⁹ A zeolite composite material for environmental odor control is useful in controlling odors from waste, for example, as an alternative daily cover for landfills and in the composting applications.¹⁷²

Landfill odors have created a major concern for the Chinese public.¹⁷⁰ The average radius of impact of landfill odors in China is 796 m.¹⁷⁰ The total land area impacted by odors has reached 837,476 ha, accounting for 0.09% of China's land territory.¹⁷⁰ In Italy, the risks are much lower than those accepted by the international agencies.¹⁷¹ Odor is significant for a limited downwind area near the landfill.¹⁷¹

9.24 LAMINATES

Laminated composite absorbent having odor control features has absorber gelling material.¹⁷³ There are two absorbing layers: one working when not wetted, the other working when wetted.¹⁷³ Dry condition agents include chlorophyll particles, activated carbon granules, charcoal, ion exchange resin, activated alumina, zeolites, including molecular sieves.¹⁷³ Wet condition agents include hydrolyzed acrylonitrile grafted starch, acrylic acid grafted starch, polyacrylates, and maleic anhydride-based copolymers.¹⁷³

An odor control substance contains a plurality of fibers oriented in z-direction and odor control coating applied to the fibrous substrate.¹⁷⁴ The majority of coating resides on the exposed portion.¹⁷⁴ Nonwoven web material can be made from polyolefins, polyamides, polyesters, polycarbonates, polystyrenes, fluoropolymers, vinyl polymers, and their blends.¹⁷⁴ Odor control coating contains activated carbon, zeolites, silica, clays, alumina, magnesia, titania, cyclodextrin, and their combinations.¹⁷⁴ Coating also contains a binder which becomes insoluble in water upon crosslinking.¹⁷⁴ Examples of such crosslinking agents include dimethylol urea-melamine-formaldehyde, urea-formaldehyde, and polyamide epichlorohydrin.¹⁷⁴

Odor controlling liner is a composite material comprising a water-impermeable layer, sandwiched between the water-impermeable and water-absorbent layer.¹⁷⁵ Odor absorbent is a part of the water-absorbent layer.¹⁷⁵ Odor absorbents include baking soda, activated charcoal, and the like.¹⁷⁵

An antimicrobial, odor control composite contains film with fabric laminated on both sides.¹⁷⁶ The film is a breathable film layer with a measurable gas or vapor transmis-

sion rate.¹⁷⁶ It contains metallic silver, zinc and copper ions and it is combined with fabric or foam to form an antimicrobial, odor, and infection control laminated structure.¹⁷⁶ The polymers used in the thermoplastic film include polyurethane, ether amides, or block copolyesters.¹⁷⁶

9.25 LEATHER

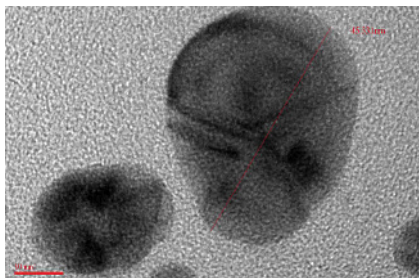


Figure 9.5. TEM image of particle (bar=10 nm). Adapted, by permission, from Velmurugan, P; Lee, S-M; Cho, M; Park, J-H; Seo, S-K; Myung, H; Bang, K-S; Oh, B-T, *Appl. Microbiol. Biotechnol.*, **98**, 8179-89, 2014.]

A burned odor characteristic of lased leather is subjected to heating and to a forced gas flow.¹⁷⁷ This treatment is able to reduce burned odor.¹⁷⁷

Lasers have been used to mark (etch) or cut leather products.¹⁷⁸ A distinctive odor is caused by burning leather with a laser.¹⁷⁸ The odor caused by laser processing can be substantially reduced by heating the material to a temperature of 150°C.¹⁷⁸

Silver nanoparticles (Figure 9.5) were produced using a natural polymer pine gum solution as the reducing and capping agent.¹⁷⁹ The nanoparticles were applied to leather to obtain antibacterial properties.¹⁷⁹

9.26 MEDICAL

Odor-absorbing web material contains a porous base web (e.g., fibrous nonwoven or paper) with odor-absorbing particulate such as zeolite distributed throughout.¹⁸⁰ Alkaline salt or alkaline earth oxide particulate are also distributed throughout to better effect removal of acidic malodor.¹⁸⁰ These absorbing particulates are attached to fibers by a binder.¹⁸⁰

Cellulose fibers are treated with an acidic odor control agent to produce odor controlling system.¹⁸¹ The odor system absorbs odor and inhibits the formation of various odor-producing bacteria.¹⁸¹ The system is used in personal care and medical absorbent garments. Cellulose fibers are treated with a transitional metal-containing compound, such as oxide, hydroxide, or carbonate.¹⁸¹ Odor control agents include dicarboxylic acids, tri-carboxylic acids, and higher polycarboxylic acids, such as, for example, citric, maleic, and tartaric acid.¹⁸¹

Medical food tablets containing free amino acids, vitamins, minerals have improved taste and aroma.¹⁸² Tablets have reduced odor and off-flavors when the amino acid blend or at least the portion of the blends most responsible for such odor and off-flavors is dry-blended into the formulation.¹⁸² It has been found that these amino acid solids, which most typically appear as solid crystals within the tablet, have reduced odor and flavor as compared to those which were spray dried.¹⁸²

A method of delivering a fragrance to medical apparel has been patented.¹⁸³ Every fibrous material used in making a facemask has some intrinsic odor.¹⁸³ The quality and intensity of odor vary from package-to-package and batch-to-batch.¹⁸³ Facemasks are scented *in situ*.¹⁸³

A system for removing dimethyl sulfoxide contains adsorbent, odor absorbing fabric, masks, clean air members, and clean air supply assemblies.¹⁸⁴ Odor capturing fabrics contain polyamines.¹⁸⁴ Adsorbing core particles are selected from a group of activated carbon, inorganic oxide, a compound having ion exchange capacity, an ion exchange resin, and a chemical deodorizer.¹⁸⁴ Odor-eliminating fibers also contain an odor-eliminating component, such as silver or copper.¹⁸⁴

Cellulosic fibers have odor control characteristics.¹⁸⁵ Odor-inhibiting agent may contain biocide and urease inhibitor.¹⁸⁵ The formulation also contains a liquid carrier.¹⁸⁵ The cellulosic fiber is impregnated with an odor-inhibiting formulation.¹⁸⁵ The resultant product is useful for making absorbent articles with odor-inhibiting characteristics.¹⁸⁵ The fiber prevents the growth of microorganisms and production of ammonia.¹⁸⁵

Polymer-cyclodextrin composite nanofibers, by virtue of the hollow cavities and abundant hydroxyl groups present in cyclodextrin, could potentially be an ideal substrate for removing wound odors through formation of inclusion compounds with odorants, while providing an ideal environment for the wound to heal.¹⁸⁶

The odor absorbent of poly(vinylidene chloride) can be used in ostomy pouches and other medical products.¹⁸⁷

9.27 MEMBRANES

A portable liquid purifying device has an activated carbon filter and a membrane filter.¹⁸⁸ When the liquid has an offensive odor or odor of sterilizer (e.g., hypochlorous acid), the odor can be effectively removed by activated carbon.¹⁸⁸

Polytetrafluoroethylene membrane contains carbon particles and has excellent absorption, odor resistance, and air permeability.¹⁸⁹ It is obtained by mixing porous carbon particles with a porous resin and a solvent, which easily dissolve in water, with distribution of the composite uniformly on the surface of polytetrafluoroethylene membrane by coating or dipping, drying out the membrane to remove the solvent and adhering the composite to the surface of the membrane.¹⁸⁹

The membrane is prepared from the sulfonated block copolymer.¹⁹⁰ The process of production should not cause formation of offensive odor. Isobutyric acid is formed from isobutyryl sulfate generation and reaction.¹⁹⁰ The residual carboxylic acid is converted to an ester, which is volatile therefore easy to remove.¹⁹⁰ In addition, the ester does not impart an offensive odor because methyl and ethyl isobutyrate are often used as fragrance additives, whereas acid causes the formation of an offensive odor.¹⁹⁰

A membrane device was developed for the release of volatile compositions, such as volatile fragrances and deodorizing compositions.¹⁹¹

9.28 OIL SANDS

Naphthenic acids occur naturally in various petroleum oils and in oil sands tailings waters and have been implicated as potential fish tainting compounds.¹⁹² Trained sensory panels were used to determine the odor detection thresholds of two commercial naphthenic acid preparations and naphthenic acid extracted from oil sands.¹⁹² Analysis of the three naphthenic acid preparations by gas chromatography-mass spectrometry showed that each had a unique distribution of acids.¹⁹² And apparently these differences affect their odors

because the sensory panel found large differences between the odors of the tested samples.¹⁹²

Odors of naphthalene, 1-methylnaphthalene, 2,6-dimethylnaphthalene, 2,3,5-trimethylnaphthalene, 1,4-dimethylbenzene, benzothiophene, dibenzothiophene, and 2,5-dimethylphenol were analyzed as possible fish tainting substances.¹⁹³ Results demonstrate that substantial variability was typical for 11 panelists involved, who were selected for their sensitivity and consistency, while method uncertainty was tolerably narrow.¹⁹³

In 1993 the Athabasca River received effluent from one bleached kraft pulp mill, three chemithermomechanical pulp and paper mills, one oil sands extraction, and a number of municipal effluents.¹⁹⁴ Mill effluent was detectable for more than 950 km downstream from the mill and this effluent was the major source of odor to the Athabasca River.¹⁹⁴ The oil sands effluent (downstream of Fort McMurray) was recognized as very distinctive and relatively strong, but with the possible exception of a sulfur descriptor it was difficult to recognize any impact of this effluent on the Athabasca River after dilution.¹⁹⁴ It is now considered that sulfur dioxide, fugitive volatile organic compounds, and a variety of sulfur-inorganic and -organic compounds (total reduced sulfur), can be a source of odor in Wood Buffalo in Athabasca Sands Region.¹⁹⁵ The organic fraction of total reduced sulfur in the most odiferous.¹⁹⁵

9.29 PAINTS AND COATINGS

Coalescing aids are being taken out of the formulations to reduce/eliminate VOC contents of coatings as a response to regulations and interest in low odor coatings.¹⁹⁶ Film forming properties need to remain identical, therefore binder polymers that exhibit low minimum film formation temperatures are developed.¹⁹⁶ Such changes in binders have a negative impact on freeze-thaw stability and open time.¹⁹⁶ Additive FT-100 and Additive OTE-500 were designed to solve these issues.¹⁹⁶ They are added either to resin or paint and five cycles of freeze-thaw stability and significant extension in open time are achieved.¹⁹⁶

The odor emitted from paint drying processes could be eliminated by $\text{CuO-Co}_3\text{O}_4\text{-CeO}_2$ (Cu:Co:Ce = 10:45:45) catalyst.¹⁹⁷ Volatile organic compounds present at ppm levels were decomposed over the catalyst.¹⁹⁷ Using a semiconductor odor sensor, the odor level in the front and rear of the reactor was determined.¹⁹⁷ The odor level was decreased by 95%.¹⁹⁷

Isocyanatocyclohexane and isothiocyanatocyclohexane are found in urban and industrial air.¹⁹⁸ They are used in the automobile industry and in building insulation, as well as in the manufacture of foams, rubber, paints and varnishes.¹⁹⁸ The concentrations ranged between 246 and 29 $\mu\text{g m}^{-3}$ for isocyanatocyclohexane and isothiocyanatocyclohexane, respectively, for industrial areas.¹⁹⁸ In urban and residential locations concentrations ranging between 164 and 29 $\mu\text{g m}^{-3}$ for isocyanatocyclohexane and isothiocyanatocyclohexane, respectively, were determined.¹⁹⁸

Entrapping agent, such as cyclodextrin, is used to entrap odorous substances from an aqueous latex-based coating material.¹⁹⁹ This method can be used in coatings such as stains, sealants, nail polish, and paints.¹⁹⁹ During their manufacture by-product molecules, such as acetates, short chain aldehydes, ketones, and fatty acids, are formed from binder.¹⁹⁹ They are responsible for distinctive and often undesirable odor of paints experi-

enced by user both on opening container and during the painting.¹⁹⁹ Cyclodextrin is suitable to deal with this odor problem. In addition to cyclodextrin, zeolite is also added.¹⁹⁹

The method of reducing odor from latex paints includes addition of stabilizer, biocide, and thickener.²⁰⁰ Stabilizer is 4-hydroxy-2,2,6,6-tetramethylpiperidinoxyl, hindered phenol, hindered amine, unsaturated fatty acid nicotinamine, thiodicarboxylic acid, or N,N-dialkylhydroxylamine.²⁰⁰ Biocide is 2-methyl-4-isothiazolin-3-one or 2-n-octyl-4-isothiazolin-3-one.²⁰⁰ Thickener is polyurethane, hydroxyethyl cellulose, carboxymethyl cellulose, modified alkali-soluble emulsion polymer, or hydrophobically modified hydroxyethyl cellulose.²⁰⁰

Low odor latex paint is capable of reducing interior odors.²⁰¹ Various odors are associated with latex paints.²⁰¹ The odors may arise from buffers, solvents, biocides, thickening agents, or crosslinking agents.²⁰¹ Also, the binder may be decomposed as described above. In residential and commercial buildings odors are the result of cooking, cigarette smoke, pet odors, mold and mildew growth, etc.²⁰¹ The indoor odors can be reduced by air fresheners, scented candles, air purifiers, ionizers, ozonizers, and electrostatic filters.²⁰¹ But these methods of reduction or masking odors only work temporarily.²⁰¹ The latex paint of this invention contains an odor absorbing agent, such as zeolite, cyclodextrin, sodium bicarbonate, or activated carbon.²⁰¹ Odor neutralizing agent such as sodium bicarbonate, undecylenic acid, its salts and esters, chloramine T, or zinc ricinoleate, can also be added.²⁰¹ Other materials, such as nano-titanium dioxide, zinc oxide, or anatase titanium dioxide, which are capable of degrading odors in the presence of light, can also be added.²⁰¹

Low odor coating composition comprises emulsion-polymerized addition polymer, carboxylesterase (enzyme), and carboxylesterase deactivating agent.^{202,203} The carboxylesterase is employed to minimize the free carboxyl ester content in the composition, which is the essence of the low odor composition.^{202,203} The carboxylesterase is deactivated *in situ* in order to minimize the residual carboxylesterase activity.^{202,203}

Ecological wall paint (Frischeweiss developed by Auro) degrades pollutants and odors by photo-catalytic effect.²⁰⁴ This emission-free paint also inhibits microorganisms such as mold spores, viruses, and bacteria.²⁰⁴ Ninety percent of the formaldehyde degrades after 1 hour, and 95% after 2 hours.²⁰⁴

Paint manufacturing waters can be successfully treated by coagulation/electrochemical methods to remove odor, organic load, and other important contaminants of water.²⁰⁵ The estimated cost of energy required to remove the organic load was 6.09 kWh/m³.²⁰⁵

Aminoalcohol compounds can be used as low odor, zero or low volatile organic content additives for paints and coatings.²⁰⁶

9.30 PAVEMENT

Airborne emissions, pollutant release over time, and odor production related to asphalt laying have been determined and compared in relation to the amount of recycled material.²⁰⁷ The trend observed (decrease in odor with increasing recycling rate) is directly linked to the mass of new additional bitumen.²⁰⁷

Antistripping additive substantially reduces the odor of asphalt compositions.²⁰⁸ It consists citrus terpene (D-limonene), vegetable oil, and silicone oil. It is mixed with both asphalt and aggregate.²⁰⁸

A method of control of emissions during asphalt paving has been patented.²⁰⁹ The method includes spraying asphalt on a surface while moving over the surface and releasing the liquid agent so that both mix together.²⁰⁹ The patent includes a schematic diagram of vehicle equipment used in this application.²⁰⁹

A low odor asphalt composition contains aldehyde- and ketone-containing compounds.²¹⁰ Undesirable odors from hot asphalt are reduced by the composition without adversely affecting properties of asphalt.²¹⁰ Aldehyde- and ketone-containing composition can be added to molten or semi-molten asphalt to produce a low odor asphalt composition.²¹⁰ Suitable aldehydes include 2-chlorobenzaldehyde, α -methylcinnamaldehyde, 4-anisylaldehyde, verbenaldehyde, vanillin, and many other.²¹⁰ Suitable ketones are camphor, isophorone, isobutyrophenone, propiophenone, benzophenone, fluorenone, and many other.²¹⁰

The road and airport pavement construction is a polluting factor for greenhouse gas and odor emissions.²¹¹ Up to 65% of CO₂ emission were saved by using the recycled pavement having comparable performance to a standard asphalt pavement.²¹¹

Hydroxylated carboxylic acid salts which contain at least 17 carbon atoms, such as zinc ricinoleate, act effectively as deodorants in asphalt and asphalt containing compositions.²¹² The deodorant is used in a concentration of, at least, 0.1 wt%.²¹²

9.31 PHARMACEUTICAL PRODUCTS

Irradiation is used as a means of sterilization of packaging containers for aseptic packaging of food, pharmaceutical or cosmetic products.⁶⁰ Irradiation is performed using γ -rays from ⁶⁰Co.⁶⁰ Twenty nine characteristic odorants in a non-irradiated control sample and 38 odorants in γ -irradiated polypropylene samples were found.⁶⁰

The electronic nose was used to evaluate coated tablets for unpleasant odor.²¹³ Tablets contained L-cysteine, an unpleasant odor component. The odor-masking ability of thin-layer sugarless coating was studied.²¹³ The thin-layer sugarless coated tablets have excellent masking ability of the unpleasant odor, equivalent to that of sugar-coated tablets due to the dense coating layers.²¹³ The formulation contained erythritol 20.1%, talc 10.6%, TiO₂ 0.8%, microcrystalline cellulose 1.9%, powdered acacia 4.6% and purified water 62.0%.²¹³

A coating for masking or reducing the odor of pharmaceutical preparations contains Valerian extract, hydroxyalkyl cellulose, methacrylate copolymer, sugar, and anti-tackiness agent.²¹⁴ The coating is applied three times, with each coating having a different formulation.²¹⁴

A pharmaceutical vessel is a scented plastic composition which is placed inside the pharmaceutical container.²¹⁵ Some pharmaceutical products have an unpleasant odor, for example, fish oil capsules.²¹⁵ The scenting material can be chosen from a large variety of products.²¹⁵ It should be oil-soluble to mix well with a polymeric binder.²¹⁵

A pharmaceutical formulation for sulfur-containing drugs in liquid dosage form has an odor-masking agent.²¹⁶ Any flavoring agents or their combinations can be used in this invention.²¹⁶ The flavoring agents can be natural, fruit flavor, or synthetic flavors.²¹⁶

A pharmaceutical package reduces the odor of preparation.²¹⁷ Odor from preparation is continuously generated as medoxomilester is hydrolyzed, so the package has to be capable of continuous removal of the odor.²¹⁷ Salts of inorganic and organic bases are used for

removal of odor.²¹⁷ Inorganic bases include alkali metals such as sodium and potassium or alkaline earth metals such as zinc, iron, or copper.²¹⁷ The organic bases include amines, such as trimethylamine, triethylamine, pyridine, picoline, and the like, or basic aminoacids such as arginine, lysine, or ornithine.²¹⁷

Pharmaceutical excipients containing volatile odor-active molecules can be used in pharmaceutical development to increase patients' compliance.²¹⁸ The challenges include a selection of proper composition and potential changes during storage.²¹⁸

9.32 PHOTOGRAPHIC MATERIALS

A method of treating photographic waste solution for inhibiting bad odor production has been proposed.²¹⁹ Heating and evaporation cause formation of bad odor due to the production of sulfurous acid, hydrogen sulfide, ammonia, ammonium thiosulfate, ammonium sulfite, and amine compounds.²¹⁹ The goal of elimination of bad odors is achieved by oxidation in the presence of a catalyst, careful control of pH throughout the process, and a complex device which is described in detail in the patent.²¹⁹

A photographic fixing composition for processing silver halide photographic material comprises a fixing agent, a sulfite stabilizer, an acid and a buffer.²²⁰ Odor associated with fixers is due to sulfur dioxide produced by disproportionation of sulfite.²²⁰ The release of sulfur dioxide from fixing composition is inhibited and the resulting odor eliminated by regulation of pH drop on dilution with water.²²⁰

The odorless fixing solution for fixing silver halide in photographic media includes ammonium thiosulfate as a halide solubilizing agent and a non-volatile organic acid for pH buffering.²²¹ The preferred acid is a glycolic acid, succinic acid, or their derivatives.²²¹

The current invention provides the option to add a desired odor to the selected digital image files and form a digital image which contains odor information.²²² When browsing the digital image files containing odor information, the odor can be dispersed through an odor dispensing unit.²²²

9.33 PIPES

The most important problem with odor in pipes is related to the use of synthetic materials, which generate odorous substances which are then transferred to drinking water and change its quality.²²³ In addition to pipes, membranes, organic coatings, and epoxy relining products may cause the formation of odors in drinking water.²²³

Epoxy lined copper pipes are used to remediate corroded plumbing. Panelists repeatedly and consistently described a "plastic/adhesive/putty" odor in the water from the pipes.²²⁴ The odor intensity remained relatively constant for each of two subsequent flushes.²²⁴ Water exposed to the epoxy liner for 72–96 h stagnation times also showed a significant increase in TOC (0.4–0.6 mg/L) and a severe decrease in both free chlorine and monochloramine residual.²²⁴

The leaching of polyvinylchloride pipe and its joints, primer, and cement, into drinking water distribution system was studied.²²⁵ PVC primer and cement leached alone and/or when applied to gray or white PVC pipes producing a glue/varnish odor.²²⁵ Solvents and their reaction products that formed during the bonding process on the PVC pipe were

a primary source of the glue/varnish odor.²²⁵ Acetone, tetrahydrofuran, methyl ethyl ketone, and cyclohexanone had a glue/varnish odor.²²⁵

Hydrogen sulfide oxidation on sewer pipe surfaces was investigated in a pilot scale experimental setup.²²⁶ Sulfide related concrete corrosion and odor are often observed.²²⁶ Hydrogen sulfide oxidation was approximately two orders of magnitude faster on the concrete pipe surfaces than on the plastic pipe (HDPE and PVC) surfaces.²²⁶ Removal of the layer of reaction (corrosion) products from the concrete pipes was found to reduce the rate of hydrogen sulfide oxidation, but the rate of sulfide oxidation was restored to its background level within 10–20 days.²²⁶

The sensory panel attributed a weak to moderate intensity of a “waxy/plastic/citrus” odor to the water from the HDPE pipes but not the chlorinated PVC samples.²²⁷ Water stored in both types of pipe showed disinfectant demands of 0.1–0.9 μg disinfectant/ cm^2 pipe surface, with HDPE exerting more demand than chlorinated PVC.²²⁷

Migration of volatile organic components from plastic pipes (HDPE, PEX, and PVC) into drinking water was studied.²²⁸ 2,4-Di-*tert*-butyl-phenol, which is a degradation product of antioxidants such as Irgafos 168, was the major migrating component of HDPE pipes. Also, esters, aldehydes, ketones, aromatic hydrocarbons, and terpenoids were identified as migration products from HDPE pipes. PEX pipes showed that VOC migrated in significant amounts into the test water.²²⁸ Oxygenates predominated VOC in the case of PEX pipes.²²⁸ PVC pipes produced few volatile migrants and no significant odor of the test water.²²⁸

Ethyl-*tert*-butyl ether and methyl-*tert*-butyl ether odorants were found in PEX pipes. Free chlorine caused odor levels for PEX pipe to increase from 26 to 75 threshold odor number.²²⁹ The odor remained greater than the USA's Environmental Protection Agency's the secondary maximum contaminant level.²²⁹

9.34 PLUMBING MATERIALS

Biological and chemical sources can be interrelated as organic matter leaching from plumbing materials may provide a medium for microbial growth.²³⁰ Additionally, the interaction between types of disinfectant with each other, pipe surfaces and other chemical constituents in the distribution system have to be considered.²³⁰ Synthetic plumbing materials have the ability to generate taste and odor in drinking water in several ways: direct leaching of volatile organic compounds from the polymer, microbial growth resulting from the available leached polymer acting as a substrate, and polymer permeation and the reaction of disinfectants with organics in the pipe.²³⁰ Drinking water systems include pipes, valves, fittings, and other plumbing materials, each of which can contribute to the production of odors by its own way.²³⁰

9.35 ROOFING

The composition contains odor-emitting hydrocarbonaceous material and odor suppressing the amount of an aldehyde or ketone and carboxylic acid ester.^{231,232} The material is used as a roofing material based on asphalt.^{231,232} The aldehydes that are useful in this invention include formaldehyde, acetaldehyde, propionaldehyde, *n*-butyraldehyde, and many other aldehydes.^{231,232} Ketones useful in the invention include acetone, methyl ethyl

ketone, mesityl oxide acetophenone, and many other common ketones.^{231,232} The carboxylic ester group include methyl acetate, ethyl formate, ethyl acetate, ethyl butyrate, soy methyl ester, and many other esters.^{231,232}

Two specific types of additives are added to cold and hot melt asphalts to reduce or complex obnoxious, toxic odor: complexing agents and fragrances.²³³ Dialkylglycol alkyl ethers and dialkylphthalates are used as complexing agents.²³³ Lemon, orange, peppermint, spearmint, and cinnamon oils are added as fragrances.²³³

The additives designed to remove odor from roofing material include essential oil and its components.²³⁴ Traditional odor-treating compositions act as deodorizers or masking agents.²³⁴ Such techniques are poor at masking strong odor.²³⁴ Substances proposed in this invention fall into the following categories: terpenes, alcohols, aldehydes, aromatics, phenolics, and esters.²³⁴ Preferred odor reducing additives are terpenes.²³⁴ Useful terpenes include rosemary, cedarwood, eucalyptus, clove, thyme, and lavender oils, and α - and β -pinenes, cineole, camphor, terpineol, bornyl acetate, thymol, and many others.²³⁴

Fungi resistant asphalt and asphalt sheet materials contain an odor-reducing additive to neutralize the asphalt odor.²³⁵ Such additive is essential to plant oil added in an amount of 1 wt%.²³⁵

9.36 SEALANTS

Hexane and dimethyloctanol isomers found among different VOCs in the building were traced to sealants.²³⁶ The odor intensity of the emissions from the building products only decayed modestly over time.²³⁶

A large number of different odorants were emitted from acrylic, water-based sealant, including: acetone, 2-propanol, 2-methyl-2-propanol, butanal, 2-methyl-1-propanol, butanol, acetic acid, butyl acetate, 1,2-ethanediol, 1,2-propanediol, butyl propionate, 2-butoxyethanol, ethoxyacetic acid, 2-ethylhexanol, 2-(2-butoxyethoxy)ethanol, 2-(2-butoxyethoxy)ethanol acetate, pentadecane, hexadecane, bis-(1-methylpropyl) malonate, bis-(1-methylpropyl) succinate, bis-(1-methylpropyl) adipate.²³⁷

A window sealant from saturated alkanethiol adduct of polybutadiene or polyisoprene does not contain sulfurous odor and has low VOC content.²³⁸ To avoid sulfurous odor, alkanethiols must have from 8 to 20 carbon atoms.²³⁸

A method for producing mercaptan terminated liquid polymers with increased chemical reactivity and the reduced odor was disclosed.²³⁹ It involves heating the polymeric material under a condition which does not permit oxidation and depolymerization while removing at least 50 wt% of low molecular weight mercaptan compounds to produce stripped material.²³⁹ Typical low molecular weight mercaptan compounds include α,ω -dimercaptodiethylsulfide, α,ω -dimercaptodiethyl ether, 1,8-dimercapto-3,6-dioxaoctane, 1,2-dimercaptoethane, dimercaptodiethyl formal, dimercaptomethyl diphenyl ether, 2-mercaptoethanol, 2-mercaptopropanol, 3-mercaptopropanol, 3-mercaptobutanol, and 4-mercaptobutanol.²³⁹ The preferred temperature of stripping is 135-175°C under vacuum of 1-100 mm Hg.²³⁹ The operation usually takes 2 min.²³⁹

One component sealant based on dispersion of vinyl polymers is in wet state substantially free of VOC.²⁴⁰ Preference is given to acrylates based on 2-ethylhexyl acrylate and butyl acrylate.²⁴⁰

A tire sealant is designed to plug a puncture to a pneumatic tire mounted on a rim by filling tire with sealant, followed by filling the tire with pressurized air, and rotating the tire to distribute sealant.²⁴¹ Acids can be added to the tire sealant to lower pH to 7.²⁴¹ The neutral pH slows action of bacteria and reduces odor.²⁴¹

The tire puncture sealant is based on urethane emulsion or polyolefin emulsion and an antifreezing agent having a hydrogen ion exponent of 5.5 to 8.5.²⁴² This antifreezing agent has a less pungent odor than normally expected from tire puncture sealant.²⁴²

Liquid sealant has been developed for odor suppressing seals in waterless urinals.²⁴³ Sealant contains 1 wt% Dowacide as odor control agent.²⁴³ Other odor control agents include triazines, hydantoins, and parabens.²⁴³ Pine oil is the preferred fragrance.²⁴³

Room temperature vulcanizable composition containing organosiloxane or polyurethane units having at least one terminal methyl isopropyl ketoximine moiety has been invented.²⁴⁴ These type of sealants usually have unpleasant odor because of the type of crosslinkers used in application. It was found that silanes having bis-, tris-, or tetrakis-methyl isopropyl ketoxime or methyl propyl ketoxime functionality are effective crosslinkers and they cause only a relatively short duration of odor emission that occurs during curing.²⁴⁴

The aromatic diamine curative Ethacure 300 has greatly reduced the odor of the liquid product, which is used in both hot and room-temperature polyurethane cast elastomers and sealants.²⁴⁵ Polyamine containing two secondary amine groups and three benzene rings has low odor in applications as epoxy hardener.²⁴⁶

9.37 SOFT DRINKS

Mineral water and soft drinks with a perceptible off-odor were analyzed to identify contaminants originating from previous misuse of the refillable polyethylene terephthalate bottle.³¹ The origins of the off-odors are caused by previous consumer misuse of food products (liquorice-flavored alcohol, home-made alcohol containing fusel oil) or non-food products (cleaning products, petroleum products, oral moist snuff and others).³¹

There were relatively large differences between the assessments of the same orange-based carbonated soft drinks by the same assessors in the different replicates.²⁴⁷ The results of profiling of orange-based lemonades by nearly untrained assessors should be considered with some reserve.²⁴⁷

Retinol (vitamin A) from fortified unrefined sugar was almost completely lost in the production of soft drinks, largely because of its adsorption onto activated carbon and diatomaceous earth that are used to reduce color and to eliminate odors and organic impurities in the purification process.²⁴⁸

A soft drink container has a plurality of the additive storage containers and a mechanism to release the additives into the base liquid storage.²⁴⁹ One of these additive storage containers is used for storage of odor chemicals.²⁴⁹ When various additives in storage containers are mixed together, they may cause biochemical reactions to take place inside the soft drink, resulting in volatilizing fresh taste and odor, which may turn offensive.²⁴⁹

The spoilage of soft drinks by yeasts is accompanied by carbon dioxide production, which may cause bulging and burst of a bottle, excessive effervescence when opening the bottle, turbidity, sediments, production of undesirable flavor and aroma compounds, such

as “fruity”, “keto”, and “alcoholic” odors.²⁵⁰ Also significant decrease in total soluble solids in soft drinks spoiled by yeasts is observed.²⁵⁰

9.38 TIRES

A fragrant powder is used in the production of fragrant tires to prevent bad odor of tire during sudden start, acceleration, and brake, which all generate strong smell.²⁵¹ The fragrant powder composition includes fragrance(s), solvent, and porous silica.²⁵¹ The loss of fragrance is diminished by combining it with porous silica.²⁵¹

Modified natural rubber has polar groups grafted to natural rubber, which is then combined with carbon black and/or silica.²⁵² Natural rubber (without such modification) produces odor when mixed with reinforcing fillers.²⁵² Presence of polar groups helps to capture odor compounds, which decreases the odor during processing.²⁵²

A method of capturing organoleptic odor has been developed.²⁵³ A functional additive has odors from a plurality of organoleptic sources and it is blended with odor control agent and resin. The odor control agent is selected from a group, including nephelite syenite, silica gel, hydrogels, hard and soft clays, bentonite, clinoptilolite, hectorite, cerium, cesium, chabazite faujasite, gmelinite, brewsterite, calcium silicate, hydrotalcite, zinc or magnesium aluminum hydroxy carbonate, zinc oxide, zinc hydroxide, zinc carbonate, calcium oxide, calcium hydroxide, calcium carbonate, potassium meta-phosphate, silver oxide, magnesium hydroxide, magnesium oxide, copper oxide, ferric and ferrous oxides, sorbitol, glucitol, mannitol, glucose, dextrose, dextrin, allophates, silica, sodalite, silicon oxide, aluminum oxide, natural zeolites, manganese dioxide, nano zinc oxide, or nano titanium.²⁵³ The addition of the odor control agent reduces the level of volatile and semi-volatile organic compounds that come off the mixture of the resin and functional additive.²⁵³

RODO[®] 0 from Vanderbilt Chemicals LLC neutralizes typical rubber odors.²⁵⁴ One to 3 wt% of crumb rubber is sufficient to deodorize tire crumbs.²⁵⁴ A pneumatic tire has wear indicator which is composed of microcapsules containing a fragrant chemical which emits odor not normally associated with the tire.²⁵⁵

9.39 TUBING

A multilayer odor barrier tube for a fecal drainage catheter is coextruded.²⁵⁶ If the collection bag into which the catheter tube drains lacks odor barrier properties, unpleasant odors escape the collection bag, negating the benefits of a multilayer catheter.²⁵⁶ The odor barrier has 30% thickness of total multilayer wall, and it is made from polyamide.²⁵⁶

9.40 WATER

Odor and taste change in water is mostly related to pipes and plumbing systems as discussed in Sections 9.33, 9.34, and 9.39. We analyze here information which was not included in these three sections.

The odor of the drinking water was described by local people in South America as “olive odor” and as green apple, fruity and olive oil by panelists.²⁵⁷ The main odor was caused by 2-ethyl-5,5-dimethyl-1,3-dioxane, but *cis* and *trans* isomers of 2-ethyl-4-methyl-1,3-dioxolane were also identified.²⁵⁷ These compounds had been spilled by a polyester resin manufacturing plant.²⁵⁷

The best method of ozone oxidation to decrease the taste and odor of the water from the Eagle Gorge Reservoir was studied by solid phase microextraction and flavor profile analysis.²⁵⁸ Ozone caused oxidation of the following odorants: *cis*-3-hexene-1-ol, *trans*,*trans*,-2-4-heptadienal, *cis*-3-hexenyl acetate, 2-isopropyl-3-methoxypyrazine, 2-methylisoborneol, geosmin, and heptanal.²⁵⁸ Ozone dose is the most important factor in determining the removal of geosmin and 2-methylisoborneol.²⁵⁸

γ -Radiation doses of 5 and 10 kGy (food irradiation approved doses) induced no statistically significant changes in overall migration from polypropylene to water.³³ The dose of 30 kGy (sterilizing dose) induced some differences in the overall migration from PP and PVC/HDPE samples.³³ The dose of 60 kGy (special purposes sterilizing dose) induced differences in the overall migration from PP, HDPE, and PVC/HDPE samples.³³ The overall migration values were significantly lower than the limit (10 mg/dm²) set by the EU for the food grade plastics packaging materials.³³ The most radiation sensitive plastic was the HDPE/PVC from a sensorial point of view, while the more radiation stable plastics were the PET, PS, and HDPE/PA.³³

The percentage of recycled LDPE in the multilayer structure did not affect overall migration values to distilled water.²⁵⁹ Overall migration values were lower than the upper acceptable limit (10 mg/dm²) set by the European Union.²⁵⁹ Films containing recycled LDPE had no adverse effects on taste or odor of the food-contacting phase.²⁵⁹ Primary LDPE scrap may be used as a middle layer comprising 40-50 wt% of multilayer food-packaging films without any compromise in migrational, barrier, mechanical, and organoleptic properties.²⁵⁹

Cyclodextrin/epichlorohydrin copolymer was synthesized and used as an adsorbent to remove two taste and odor causing compounds, namely, 2-methylisoborneol and geosmin from Lake Michigan water.²⁶⁰ The removal efficiency of these compounds using the copolymer on average was 74.5% for 2-methylisoborneol and 77.5% for geosmin as compared to the removal efficiency using powdered activated carbon that resulted in 52.9% and 67% removal, respectively, for the same compounds.²⁶⁰

Natural organic matter is found in all surface, ground and soil waters.²⁶¹ The presence of natural organic matter causes many problems in drinking water and drinking water treatment processes, such as reduced water quality by causing color, taste, and odor problems, increased use of coagulant and disinfectant, increased biological growth in the distribution system, and increased levels of complexed heavy metals and adsorbed organic pollutants.²⁶¹ Natural organic matter can be removed from drinking water by coagulation and flocculation followed by sedimentation/flotation and sand filtration.²⁶¹

Attention has been focused on the production of musty-aroma compound such as geosmin and its impact on the quality of fresh water and water-cultured raised fish and seafood.²⁶² The rapid detection of geosmin-producing microorganisms, in particular, the genus *Streptomyces*, at early stages of differentiation, is still the best option in preventing deterioration of water quality, considering that there are no efficient means of removing these off-flavors from the water.²⁶² Electronic nose consisting of an array of 14 conducting polymer sensors was found suitable for the rapid and early detection of *Streptomyces* spores in reverse osmosis and tap water.²⁶²

Portable electronic nose has found an application for outdoor air monitoring of sewage odors.²⁶³ Metal oxide semiconductor sensors performed in discriminating between the different odors, but conducting polymer sensors were unacceptable for this application.²⁶³

The method is given to provide sterilized and odor free drinking water.²⁶⁴ The water is sterilized by ozonation and the odors are removed by incorporating zeolite in the container cap, capliner, or both.²⁶⁴ The invention also provides a container for packaging sterilized water for human consumption.²⁶⁴

Uncomplexed cyclodextrin is used for odor control.²⁶⁵ Cyclodextrin in combination with other additives provides improved antimicrobial activity.²⁶⁵

Odor blocking a water-absorbent composition comprising water-absorbent polymer and urease inhibitor. The polymer has acid groups being from 50 to 65 mol% neutralized.²⁶⁶ The urease content is from 0.0001 to 0.1 wt%.²⁶⁶

The most common taints in foods are a musty or earthy odors (commonly associated with the activity of microorganisms).²⁶⁷ The volatile compounds responsible for a moldy off-aroma include approximately 20 compounds, namely, haloanisoles, geosmin, 2-methylisoborneol, several alkyl-methoxypyrazines, 1-octen-3-ol, 1-octen-3-one, *trans*-octenol, 3-octanone, fenchol, and fenchone.²⁶⁷

UV/chlorine treatment is more efficient than UV/H₂O₂ at pH 6.5 for geosmin and 2-methylisoborneol removal.²⁶⁸ UV/chlorine efficiency is comparable to UV/H₂O₂ at pH 7.5 and 8.5.²⁶⁸ *Planktothrix* sp. is responsible for production of 2-methylisoborneol in water reservoirs.²⁶⁹

9.41 WINE

The “musty or corked” character of wine comes from the presence of 2,4,6-tribromoanisole.²⁷⁰ Also, chloroanisoles or chlorophenols are the contaminants generally reported to cause this type of defect.²⁷⁰ “Musty” off-odor was perceptible on smelling wine containing as little as 4 ng L⁻¹ 2,4,6-tribromoanisole.²⁷⁰ 2,4,6-Tribromoanisole is produced by O-methylation of its direct precursor, 2,4,6-tribromophenol.²⁷⁰ Residual pollution adsorbed on walls could be sufficient to make a building unsuitable for storing wooden barrels and plastics, as well as corks, which have been found to be particularly susceptible to contamination by the 2,4,6-tribromoanisole in the winery atmosphere.²⁷⁰

Eighty-one compounds were found to be odor-active in Californian Chardonnay wines.²⁷¹ They included the following compounds: 1,1-diethoxy ethane, ethyl propionate, ethyl isobutyrate, 2-pentanone, ethyl butanoate, 1-propanol, ethyl 3-methyl butanoate, 2-methyl-1-propanol, 2-pentanol, isoamyl acetate, 1-butanol, 2/3 methylbutanol, ethyl hexanoate, acetoin, 1-hexanol, (*trans*) 3-hexen-1-ol, ethyl octanoate, acetic acid, furfural, 2-ethyl-1-hexanol, 2-acetyl furan, propanoic acid, 2,3-butanediol (d,l), linalool, 2-methyl propanoic acid, butanoic acid, ethyl decanoate, butyrolactone, 2/3 methyl butanoic acid+furfuryl alcohol, α -terpineol, 3-methylthio-1-propanol, pentanoic acid, 2-phenylethyl acetate, β -damascenone, hexanoic acid, 2-methoxy phenol, (*cis*) oak-lactone, 2-phenyl alcohol, (*trans*) oak-lactone, (*trans*) 2-hexenoic acid, 4-ethyl guaiacol, pantolactone, diethyl malate, octanoic acid, γ -nonalactone, homofuraneol, ethyl cinnamate, eugenol, diethyl-2-hydroxy-pentanedioate, 4-ethyl phenol, 4-vinyl-2-methoxy-phenol, 4-ethoxycarbonyl- γ -butanolactone, decanoic acid, 2,6-dimethoxyphenol, diethyl tartarate, 5-hydroxymethyl-2-furfural, vanillin, acetovanillone, and 3-oxo- α -ionol.²⁷¹ Odor descrip-

tions were assigned to each of the above compounds.²⁷¹ Fruity wines high in peach, citrus, and floral terms were separated from those high in oak-related sensory attributes (oak, vanilla, caramel, spice, and butter).²⁷¹ The fruity and floral terms were associated with iso-amyl acetate, 2-phenylethyl acetate, and linalool.²⁷¹ The oaky attributes were associated with vanillin, oak-lactones, 4-ethyl guaiacol, γ -nonalactone, 2-acetyl furan, eugenol, and 2-methoxy phenol.²⁷¹

Microoxygenation is a widely-used maturation technique in red wines as an alternative to barrel aging.²⁷² It helps to remove unwanted off-odors.²⁷² It lowers herbaceous and reductive odors.²⁷² Oxygenation participates in the removal of sulfur-containing off-odors.²⁷²

Scalping of aroma compounds may affect the sensory properties of wines packed in plastic by reducing the intensity and changing the character of the original aroma.²⁷³ Ideal Fickian transport diffusional character of the phenomenon was confirmed for packages from polypropylene and linear low-density polyethylene.²⁷³ Ethyloctanoate was sorbed more into PP than LLDPE, and at much higher extent than linalool, as a consequence of the different polarity of the molecules.²⁷³ The amount of ethyloctanoate lost determines a significant variation of its odor activity value and the imbalance of the original aroma composition.²⁷³

A method of removing sulfites involves passing wine through a base anion exchange resin, then passing the wine through an acid cation exchange resin, and then treating the wine with carbon.²⁷⁴ In this process, wine, which has less than 10 ppm of sulfites is obtained.²⁷⁴

An apparatus that can automatically detect odorous substances, such as 2,4,6-trichloroanisole, in cork wine bottle stopper, has been patented.²⁷⁵ The technology is based on the electronic nose, which automatically aligns with cork stoppers to test 100% of cork wine bottle stoppers in a fast and cost-effective manner.²⁷⁵

Impurity removal system for purifying wine has been developed.²⁷⁶ Two to seven percent of wine is discarded because of contamination called cork taint.²⁷⁶ Cork taint gives to wine a musty and moldy odor.²⁷⁶ It is a reaction between chlorine left in the cork during sterilization process and phenols present in wine.²⁷⁶ This leads to the formation of trichloroanisole which affects olfactory senses.²⁷⁶ The system proposed removes odorous substances by filtration through activated carbon.²⁷⁶

Twenty-four wines were stored in strict anoxia at 50°C for 3 weeks.²⁷⁷ All wines contain bonded forms of H₂S and methanethiol (93% and 47% on average) The percentage of each decreases with age.²⁷⁷ Anoxic storage causes an increase of free forms.²⁷⁷ Both *de novo* formation and release contribute to reductive off-odors.²⁷⁷ Release is predominant for reds and H₂S, while at 50°C, *de novo* formation dominates for whites and rosés and methanethiol.²⁷⁷

Ontario icewines were fermented by different yeasts [V1116, VL1 (*Saccharomyces cerevisiae*), EC1118 (*Saccharomyces bayanus*), and spontaneous].²⁷⁸ Aroma components varied between different yeasts, for example, V1116 produced highest ethyl isobutyrate, ethyl 2- and ethyl 3-methylbutyrate, and geranyl acetone.²⁷⁸ Yeast strain impacted odor-active compounds, but its effects depended on cultivar and vintage.²⁷⁸

The ethylphenols had a masking effect on wine fruity notes.²⁷⁹ This wine defect changes the hedonic valence of the perception.²⁷⁹ The interaction between the perception

of ethylphenols and ethyl heptanoate takes place at a central locus in the olfactory system.²⁷⁹

9.42 WIRE AND CABLE

Low odor cover for a connector has been developed. It is a sleeve made of a high-density elastomeric material, such as natural or synthetic rubber. EPDM, neoprene or Hypalon rubbers are preferred.²⁸⁰ Previously used heat shrink tubing emitted a pervasive and disagreeable odor, due to the nature of dilatation solvents which have been used.²⁸⁰ In the present invention a mixture of C₇ to C₈ aliphatic hydrocarbon solvents together with fluorocarbon component is used as the dilating agent.²⁸⁰

PVC plasticizers composed of epoxidized bioesters of vegetable oil fatty acids obtained by partial transesterification with an alcohol, and glycerin and further acetylation and epoxidation were used for the production of wire and cable compounds.²⁸¹ Renewable-source plasticizers were substantially less odorous than typical for this group of plasticizers.²⁸¹

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EFFECT OF PROCESSING METHOD

10.1 BLOW MOLDING

If the amount of crosslinking agent is increased in the production of blow molding resin from polyethylene, undesirable odor is produced because of decomposition of crosslinking agent and the commercial value of the product is decreased.¹ Addition of a small amount of crosslinking agent at the time of pelletizing the high density polyethylene prepared by means of a highly active Ziegler catalyst and conducting pelletizing in the atmosphere containing a small amount of oxygen renders resin with acceptable quality regarding the odor.¹ A crosslinking agent which has a half-life period at 200°C of 1 min is preferable.¹ The amount of crosslinking agent should be in the range of 0.001 to 0.01 phr.¹ The oxygen concentration should be from 0.5 to 10 vol%.¹

A process of production of ethylene polymers that have the low formation of smoke and odor during blow molding is provided.^{2,3} The process of polymerization is conducted in a loop reactor with isobutane as diluent in a temperature range of 93-104°C.^{2,3} Polymerization is conducted with a catalyst system including chromium on support and trialkyl boron.^{2,3} The support comprises silica and titania. The catalyst system is activated at 538-704°C.^{2,3}

There is a process of blow molding a food and beverage container with a melt phase polyester layer.⁴ A protective wall is provided adjacent to the support wall and it is so positioned to isolate the product from contact with the support wall.⁴ The protective wall is formed from material which limits the migration of undesirable substances from the support wall into the food contents.⁴ Products of degradation remain entrapped within the support wall, and if they are not isolated by the protective wall, they diffuse into the contents to affect taste and odor.⁴ A protective substrate is a laminate which may include an outer adhesive layer (e.g., EVOH) and inner layer made out of PET having low acetaldehyde content.⁴ PET has better barrier properties to most odor and flavor compounds than does HDPE in the bottle applications.⁵

Thermoplastic polyester elastomer resin composition contains a glycidyl-modified ethylene-octene copolymer resin as a chain extension/hydrolysis resistance agent for blown and extrusion molding.⁶ Production of odor-causing substances such as volatile organic compounds during blow molding is reduced.⁶

Ethylene-based polymers, having a higher and a lower molecular weight components, a density greater than 0.945 g/cm³, and a melt index less than 1.5 g/10 min produce no smoke and odor during blow molding operations.⁷

10.2 CALENDERING

Ethylene-octene rubber is used to resolve the drawbacks associated with crosslinking, including the formation of odor.⁸ When used in combination with fillers, the crosslinked thermoelastic polyolefin-based elastomer has improved odor.⁸ The suitable fillers include calcium carbonate, calcium oxide, mica, talc, and their mixtures.⁸ The inorganic filler is added in the amount of 4-5 wt%.⁸

Thermoplastic elastomer composition for calender molding and sheets is obtained by heat-treating an oil-extended olefin copolymer rubber (olefin copolymer rubber and mineral oil softening agent) and polypropylene resin.⁹ Heat-treatment involves crosslinking by organic peroxide which provides a composition with less odor and staining.⁹ 2,5-Dimethyl-2,5-di(t-butylperoxy)hexane is a particularly preferred organic peroxide. The amount of peroxide is 0.01 to 0.6 wt%.⁹

Syndiotactic propylene-based polymer composition has excellent calendering formability and has improved odor characteristics.¹⁰ It contains a syndiotactic propylene- α -olefin copolymer and syndiotactic copolymers of propylene and ethylene-vinyl acetate.¹⁰ If PVC is used, the soft PVC contains a large amount of plasticizer and, thereby, color, migration and smell occur.¹⁰

A fragrance-containing coating composition for paper substrates consists essentially of a polyvinyl chloride plastisol and one or more fragrances.¹¹ The fragrance can be a fruit fragrance, a citrus fragrance, a floral fragrance, a woody fragrance, a leather fragrance, an oriental fragrance, a mint fragrance, and/or a food fragrance.¹¹ A preferred fragrance is a mixture of insect repellents present in an amount sufficient to repel insects such as flies, mosquitoes, and the like.¹¹ Natural ingredients which act as insect repellents include salicylates, benzoates, lemon and orange oils, citronella oil, geraniol, terpeneol, garlic oil, grapefruit oil, mints, southernwood, and tea tree oil.¹¹ The fragrance may include two or more components and optionally a fixative or synergistic component which increases the fragrance's odor and permits the use of smaller amounts of the fragrance component.¹¹

10.3 COIL COATING

Older technologies included solvents which were the source of odorous emissions.¹² Technological processes used 30 years ago included powder coating (no solvent emission), electrocoating (10% solvent), water-based coatings (20% solvent), high solids (50% solvent), and solvent-based systems (60% solvents).¹² Below we discuss some patents which contributed to the development of coil coating and reduction of odors.

Powder coating of substrates includes charging powder particles by friction or induction in the presence of magnetic or nonmagnetic particles, their transfer to the substrate by means of an electric field, curing, and fusing, which results in powder coating.¹³ Use of various varnishes is reported, including solvent-based, water-based, and UV-cured.¹³ Solvent-based varnishes emit solvent, water-based varnishes require substantially more energy to evaporate, and UV-curable varnishes produce odor which makes them unsuitable for food packaging.¹³ Radiation curable binder is used in this patent.¹³ These binders include unsaturated polyester, unsaturated polyacrylates, and acrylated polyesters.¹³

Photolabile 4-hydroxy-phenacyl derivatives can be used for controlled release of molecules of fragrances, UV absorbers, antimicrobials, antifogging agents, etc. from

many different substrates including coil coated materials.¹⁴ The 4-hydroxy-phenacyl derivatives are thermally stable up to 220-260°C.¹⁴ The photoproducts which are 4-hydroxyphenyl acetic acid derivatives are by far less colored and less toxic.¹⁴ Additionally, the photoproducts absorb at shorter wavelength compared to the protected intermediate, which results in a much smaller undesired filter effect.¹⁴

The invention relates to the coating material which consists of the binder mixtures, and to their use for automotive OEM finishing, automotive refinish, industrial coating, including coil coating.¹⁵ A principal problem with the known UV-curable coating materials is the surface inhibition of curing by atmospheric oxygen.¹⁵ This inhibition must be compensated by using UV lamps with a high energy density and by accelerating the cure using amine coinitiators.¹⁵ These amines frequently lead to instances of odor nuisance.¹² The invention provides the binder mixture comprising one polymer with a saturated main chain that is not polyester and one polyester having a saturated and/or unsaturated main chain.¹⁵ The coating material is used as powder coating, having short curing time and no odor problems.¹⁵

The water-dispersible polyester polymer for coil coating should be free of fatty acids (e.g., long-chain or very long-chain fatty acids), oils, and other long-chain hydrocarbons.¹⁶ The presence of such materials may impart undesirable off-tastes or odors to the packaged food or beverage products.¹⁶

10.4 COMPRESSION MOLDING

Protein-enriched thermoplastics are produced from a thermostable polypeptide, which is subjected to the process heat.¹⁷ The product (commercial name ProNectin L) can survive conditions of the compression molding, but it retains a slight odor of formic acid, which can be removed by a stream of dry nitrogen.¹⁷

Building material for interiors having odor eliminating property has been developed.^{18,20} It is achieved by the addition of hydrazide compound.^{18,20} Various attempts have been made to provide a function of capturing VOCs and eliminating odor to a gypsum-based board, but they were restricted to the elimination of formaldehyde originating from plywood and acetaldehyde from smoking.^{18,20} Broad spectrum of indoor pollutants can be eliminated by the use of the present invention in which hydrazides, dihydrazides, or polyhydrazides are employed.^{18,20}

Polyacetal resins with reduced formaldehyde odor are obtained by incorporation of an odor-reducing additive, which is low molecular weight amino compound of low volatility, succinimide, anthranilic acid, 4-amino benzoic acid, or their mixtures.¹⁹ A combination of the odor-reducing additive with a weak acidic imine was found to have a synergistic effect in further reduction of formaldehyde odor.¹⁹ Molded parts having low odor can be produced from this polyacetal by compression molding and other molding techniques.¹⁹

Flax fibres are used because of their low lignin content (~2%), which reduces thermal degradation effects, odor and discoloration.²¹

10.5 DRY BLENDING

Odor inhibitors are dry blended with olefin polymers.²² Odor inhibitors prevent odor development in olefin polymers prepared in the presence of a chromium oxide-containing catalyst and antioxidant.²² Aminophenol is used as an odor inhibitor.²² It is added in the amount of 0.01 to 2.0 wt%.²²

Activated carbon/metal oxide filter element is prepared by dry blending of an activated carbon, metal oxide, and binder to prepare filter media mixture, which is then shaped into a filter body.²³ Activated carbon term refers to a black, solid carbonaceous material, such as charcoal, bone charcoal, sugar charcoal, carbon produced from oil products, coconut carbon that remains after the decomposition of organic material by pyrolysis, and undergoes activation process.²³ Activation is typically done by exposing the material to an oxidizing agent such as steam, carbon dioxide, metal chloride (e.g., zinc chloride), phosphoric acid, or potassium sulfide, at high temperatures (800-1000°C).²³ Activation increases the absorptive capability of the carbon.²³ Metal oxide enhances the sorptive capacity of activated carbon.²³ The preferred metal oxides include Mg, Ca, and Ba.²³

10.6 EXTRUSION

Microcellular wood fiber reinforced composites show lower surface roughness and odor concentration compared to the non-foamed composites.²⁴ During foaming, the chemical foaming agent decomposes into gas and some portion of it comes out of the composite simultaneously with the odor.²⁴ It is important to note that the odor concentration levels of extruded composites are twice those of the injection molded ones.²⁴ This is because of the longer residence time of the composites inside the barrel in extrusion, which provides more time for material decomposition, with the end effect of higher odor concentration.²⁴

Problems with odor and taste in food packaging can be traced to degradation of the packaging materials during processing.²⁵ The degradation of polyethylene in a commercial extrusion coating process caused the formation of more than 40 aliphatic aldehydes and ketones, and 14 carboxylic acids, which were identified in the smoke.²⁵ The highest concentration was found for acetaldehyde.²⁵ Increased extrusion temperature from 280 to 325°C increased the amounts of the oxidized products in the smoke.²⁵ The extruded film thickness influenced the concentrations of degradation products, with the thicker film giving higher amounts of odorous products.²⁵ The recycled polymer gave lower concentrations of degradation products compared with the virgin polymer.²⁵

Low-odor microwaveable polypropylene/mica food contact articles are prepared by low-temperature processing.^{26,27} They include odor suppressing basic organic and inorganic compounds.^{26,27} The articles are free from C₈ and C₉ organic ketones which are associated with undesirable odors.^{26,27} In the past, phenolic antioxidants were used to suppress odor formation.^{26,27} Basic inorganic compound used in this invention includes calcium carbonate, typically present in a concentration of 5 to 2 wt%.^{26,27} Organic compounds useful in this application include sodium, calcium, or potassium stearate, sodium or potassium citrate, added in concentrations from about 0.5 to 2.5 wt%.^{26,27}

A propylene polymer having agreeable odor characteristics contains di-*t*-amyl peroxide and its decomposition product.²⁸ Additives, such as thioesters, which can impact odor

characteristics are avoided in resin formulations for food applications.²⁸ The most common peroxide used to control the rheology of polypropylene is 2,5-dimethyl-2,5-di-*t*-butylperoxyhexane.²⁸ Its decomposition yields several organic species such as *t*-butyl alcohol, acetone, methane, and others. FDA regulates *t*-butyl alcohol. Its upper limit is 100 ppm in food applications.²⁸ Di-*t*-amyl peroxide adequately modifies rheology but produces agreeable odor.²⁸

Low odor resin composition contains 0.1 to 10 wt% of adsorbent clay and styrenic polymer (optionally with addition of elastomeric polymer).²⁹ Adsorbent clay traps unreacted monomer and other low molecular weight materials (e.g., dimers of butadiene).²⁹ By this action, clay reduces any odor that may emanate from the article.²⁹

Styrene content is reduced in poly(arylene ether)/polystyrene blend by melt kneading carboxylic acid compound with polymers.³⁰ The method minimizes styrene monomer content in the final blend.³⁰ A previous method included removal of volatile components during extrusion.³⁰ Another source of the odor is phenol monomer, which is oxidatively polymerized to produce poly(arylene ether).³⁰ Odoriferous impurities in 2,6-dimethylphenol monomer include 2,4,6-trimethylanisole, which may be reduced by distillation of monomer.³⁰ Carboxylic acids involved include adipic, glutaric, malonic, succinic, phthalic, maleic, citraconic, itaconic, and citric.³⁰ The amount added is in the range of 0.2 to 0.5 wt%.³⁰

If a functional additive has an odor, it is blended with an odor-control agent and a resin. The blend exhibits at least a 5% reduction in odor based on a standardized odor test SAEJ1351.³¹ The odor control agent is selected from the group but not limited to: nepheline syenite, silica gel, hydrogels, hard and soft clays, bentonite, clinoptilolite, hectorite, cationic exchanged clinoptilolites, cerium, cesium, chabazite, faujasite, gmelinite, brewsterite, calcium silicate, hydrotalcite, zinc or magnesium aluminum hydroxy carbonates, zinc oxide, zinc hydroxide, zinc carbonate, calcium oxide, calcium hydroxide, calcium carbonate, potassium meta phosphate, silver oxide, magnesium hydroxide, magnesium oxide, copper oxide, ferric and ferrous oxides, sorbitol, glucitol, mannitol, glucose, dextrose, dextrin, allophanes, silica, sodalite, silicon oxide, aluminum oxide, natural zeolites, manganese dioxide, nano zinc oxide and nano titanium and their combinations.³¹

Polyether-block-amide copolymer nanocomposites based on Cloisite™ 30B exhibit stronger odor than with sodium montmorillonite.³² This may constitute a significant drawback for industrial applications despite their outstanding properties.³²

VOC emissions during processing of polyamide-6 bio-filled with technical lignin have potential for causing health issues because the main lignin emissions consist of formaldehyde and substituted phenols and benzene.³³ Polyamide-6 processed alone only emits ϵ -caprolactam.³³ Formaldehyde emissions are three times higher during the injection molding than extrusion.³³

The interfacial bonding between lignocellulosic fibers and the polymer matrix can be improved by the esterification of biomass with dicarboxylic acid anhydrides.³⁴ The main drawback of using dicarboxylic acid anhydrides is the need for separation of the organic acids formed as a by-product.³⁴ Organic acids can strongly adsorb on the composite giving bad odor.³⁴

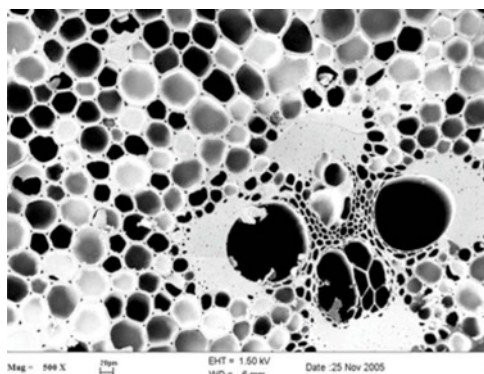


Figure 10.1. The porous structure of bamboo charcoal. [Adapted, by permission, from Ho, M-P; Lau, K-t; Wang, H; Hui, D, *Composites Part B: Eng.*, 81, 14-25, 2015.]

Re-purposed spent carbon materials were used for the production of odor-absorbing additive that can readily remove undesirable odors from a confined space.³⁵ The method of production includes extrusion of a spent carbon mixture, optionally containing diatomaceous earth, to obtain the product.³⁵

Addition of bamboo charcoal to polylactic acid composite helps to absorb odors.³⁶ Food quality can be improved as the smell can be deodorized and moisture can be maintained to reduce the growth of fungi and bacteria.³⁶ Figure 10.1 shows that bamboo charcoal owes this property to its structure having high porosity, but also because of anti-bacterial and anti-fungal properties.³⁶

10.7 EXTRUSION COATING

Extrusion coating with low density polyethylene causes emissions of aldehydes (2-prope-nal, 2-butenal, butanal, 2-methylpropanal, 2-pentenal, 2-methyl-2-propenal, 2-methylen-ebutanal, pentanal, 2-ethylacrolein, 2-ethylbutanal, hexanal, 4-methyl-3-pentanal, 4,4-dimethylhexanal, 2-hexenal, 2,3-dimethylpentanal, heptanal, octanal, nonanal, decanal, undecanal, tridecanal, tetradecanal, benzaldehyde, and pentadecanal), ketones (3-buten-2-one, 3-methyl-3-buten-2-one, 3-methyl-2-butanone, 2-pentanone, 2,3-dimethylcyclobu-tanone, 3,3-dimethyl-2-butanone, 3-penten-2-one, 3-methyl-2-hexanone, 4,4-dimethyl-2-pentanone, 3-hexanone, 3-methyl-2-heptanone, 4-ethylcyclohexanone, 5-methyl-3-hexanone, 3-heptanone, 2-heptanone, butyrolactone, 7-octen-2-one, and 6-methyl-5-hep-ten-2-one), and carboxylic acids (acetic, propanoic, butanoic, 2,2-dimethylpropanoic, pen-tanoic, hexanoic, heptanoic, and octanoic acids).³⁷ The higher the extrusion temperature, the more off-flavors and odors are produced.³⁷ More than 200 compounds were identified in fumes collected during the extrusion coating of LDPE.³⁷

Polyethylene-based coatings require extrusion temperatures that generate excessive odor and are not compatible in coextrusion with heat-sensitive polymers.³⁸ Low extrusion temperature process permits application of coextrusion to temperature sensitive poly-mers.³⁸ In the low-temperature process, polyethylene was coated in the temperature range of 204-249°C.³⁸

Encapsulation of activated carbon helps to protect the structure of the activated car-bon and preserve the odor absorbing capability of the activated carbon particles.³⁹

10.8 FOAMING

A reactive formulation is used to make a flame resistant flexible polyurethane foam with a reduced odor which is particularly suited for use in automotive applications.⁴⁰ Copper compound (cupric acetate or cupric oxide) is the odor-reducing component.⁴⁰

10.9 INJECTION MOLDING

Fragrance-emitting shaped articles such as slide fasteners which retain the various characteristics inherent to polyacetal resins have been patented.⁴¹ Polyacetal resin exposed to heat during an injection molding operation undergoes a thermal degradation process resulting in production of formaldehyde, which has an irritating odor.⁴¹ Fragrances having aldehyde groups should not be used in polyacetal because they may react with formaldehyde to produce formic acid which accelerates thermal degradation of polyacetal resin.⁴¹ The most suitable fragrances for polyacetal resin, include benzyl benzoate, ethylene brassilate, eugenol, coumarin, cinnamyl alcohol, methyl cinnamate, isoeugenol acetate, eugenol acetate, cinnamyl acetate, diphenyl ether, methyl N-methylantranilate, and ethyl methylphenylglycidate.⁴¹

10.10 JOINTING

The leaching study of the PVC pipe with its joint solvents (primer and cement) concluded that the original solvent compounds, and their reaction products that formed during the bonding process on the PVC pipe, were a primary source of the glue/varnish odor.⁴² The original primer and cement chemicals (acetone, tetrahydrofuran, methyl ethyl ketone, and cyclohexanone) had a glue/varnish odor.⁴²

10.11 PULTRUSION

The long-fiber-reinforced composite manufactured by pultrusion is used for producing uncolored or colored moldings subjected to high mechanical and thermal stress, for example, moldings in motor vehicle construction, particularly since the level of odor emission in the interior of a vehicle is very low.⁴³

Polyoxymethylenes tend to degrade when heated, particularly in an oxidative, basic, or acidic environments.⁴⁴ They emit degradation products such as formaldehyde.⁴⁴ Formaldehyde as well as other VOC emissions lead to an unpleasant odor and health hazards.⁴⁴ Low VOC emission polyoxymethylene and composition was used for pultrusion products.⁴⁴

10.12 ROTATIONAL MOLDING

Polyethylene articles are prepared by a high-temperature rotomolding process (up to 280°C).⁴⁵ The articles are white in color, have a smooth surface, and produce little or no odor.⁴⁵ Articles are stabilized with hindered amine light stabilizers and contain flame retardant.⁴⁵

10.13 RUBBER PROCESSING

The vulcanizable elastomer is processed in a mixture with clay, and it contains an odor-masking agent, such as vanilla.⁴⁶ Rubber, vulcanizing agents, and their reaction by-products may produce odors that are not pleasing to all people, particularly if objects are used in a residential environment.⁴⁶ Odor-masking agent is used in concentration from 1 to 3 phr.⁴⁶

Adhesive composition contains elastomeric latex, phenol, aldehyde, and alkylated melamine-formaldehyde resin.⁴⁷ Resorcinol is used in rubber compounds to improve adhesion to textile materials but it has offensive odor, and therefore it is not used in the composition of this invention.⁴⁷

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METHODS OF ODOR REMOVAL

11.1 OZONATION

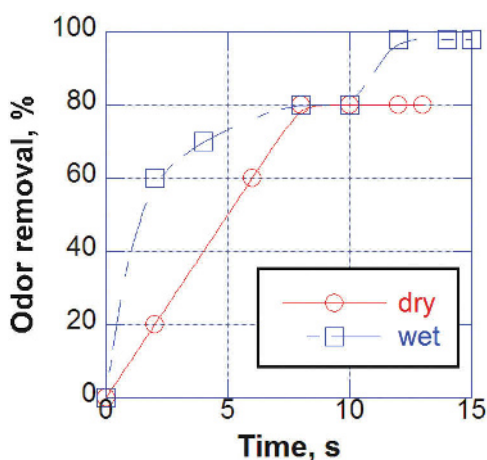


Figure 11.1. Odor removal efficiency by wet and dry ozonation. Ozone concentration 4 ppm. [Data from Perng C-H, Cheng I-L, Wang I-C, Chou M-S, *Aerosol Air Quality Res.*, **11**, 51-58, 2011.]

Removal of odorous compounds in gasses emitted from rubber processing industries has been done by ozonation.¹ The odorous gas was premixed with a selected amount of ozone-enriched air.¹ The oxidation reaction was conducted in the presence or absence of water (wet or dry).¹ Figure 11.1 shows the difference in results of ozonation.¹ Wet ozonation is certainly more effective and gives substantially cleaner air (98% of odor and 97% VOC are removed).¹

Odor removal from water is one of the major applications of this method. Ozone oxidation has been used to study the possibility of odor and taste removal from water in the Eagle Gorge Reservoir.² The results focussed on the importance and interactions between ozone dose, pH, hydrogen peroxide and contact time.²

The reservoir water was spiked with 50 to 100 ng/L of geosmin and 2-methylisoborneol and then ozonated under controlled conditions.² Ozonation proceeds very fast.² Most oxidation occurs in the first 2 min.² The higher the pH, the higher the odor detected by the odor-testing panel.² But chemical measurement showed that ozonation of odorous compounds at higher pH was slightly more effective.² Ozone dose is the most effective parameter to control the level of removal which increases with ozone level increase.²

The presence of natural organic matter affects water taste and odor. In the last 10-20 years, natural organic matter concentration in water has been increased.³ Seasonal variability in the same location and floods or droughts cause more challenges to the water purification facilities.³ Advanced oxidation processes of water treatment have emerged. These include the following combinations: O_3/H_2O_2 , O_3/UV , UV/H_2O_2 , TiO_2/UV , H_2O_2 /catalyst, Fenton and photo-Fenton processes, as well as combinations with ultrasound.³ Ozone has long been used for disinfection and taste and odor management in water treatment facilities.³ Ozone reacts with the natural organic matter by an electrophilic addition

to double bonds.³ Fast reactions occur with $\cdot\text{OH}$ -radicals that are formed when ozone decomposes in water.³ The combination of ozone with UV promotes the production of hydroxyl radicals in the ozonation process.³

The effect of slurry ozonation (combined with solid-liquid pre-separation and acidification) on emissions of odorous compounds was tested in an experimental full-scale pig growing facility using Proton-Transfer-Reaction Mass Spectrometry for online analysis of odorants.⁴ The compounds monitored included volatile sulfur compounds, amine, carboxylic acids, ketones, phenols, and indoles.⁴ The compounds with the highest removal efficiencies were hydrogen sulfide, 3-methyl-indole, phenol, and acetic acid.⁴ Based on odor threshold values, methanethiol, butanoic acid, 4-methylphenol, hydrogen sulfide and C_5 carboxylic acids are estimated to contribute significantly to the odor nuisance.⁴ The total reduction ratio fitted well with the olfactometry data.⁴ Considerable reductions of emissions were achieved by ozonation but the further reduction is needed to lower the nuisance to the neighbors.⁴ Ozone treatment of slurry may only reduce odor to a certain degree and further optimization of the system is difficult.⁴

Ozone concentrations that are several orders of magnitude greater than typical urban ambient concentrations are necessary for gas-phase ozonation of buildings, either for deodorization or for disinfection of biological agents.⁵ Ceiling tile, carpet, office partition, and gypsum wallboard with flat latex paint have large surface areas and they exhibited relatively high building ozonation by-products releases.⁵ The greatest overall building ozonation by-products mass releases were observed for three materials: paper, office partition, and medium density fiberboard.⁵ For most wall and flooring materials, building ozonation by-products mass was dominated by lighter (C_1 – C_4) carbonyls.⁵ For wood-based products, there was a greater fraction of heavier carbonyls.⁵ The release of some building ozonation by-products (e.g., nonanal) could persist for months or more after some materials are exposed to elevated concentrations of ozone.⁵

Ozonation was used for the treatment of irrigation water and special equipment was designed.⁶ Ozone and other molecules formed as a result of ozonation (hydrogen peroxide and hydroxyl radicals) have a number of beneficial uses in the treatment of irrigation water.⁶ Ozonation requires shorter reaction time than with other treatment chemicals. Ozone is highly water soluble (approximately 10 times more soluble than oxygen).⁶ When it enters water it immediately reacts, producing oxygen.⁶ Water used for irrigation has to be recycled and the major problem is related to the elimination of odors, which is also accomplished by absorption on activated carbon, ion exchange media, and other similar materials.⁶ Odorous substances include phenols, sulfur compounds, amines, aldehydes, and aromatic hydrocarbons, which are all reactive with ozone.⁶ Ozonation is also applied to the treatment of waste water using a similar approach to that discussed for the irrigation water.⁷

Portable containers can be deodorized by an invented apparatus.⁸ The apparatus has an ozone generator and air distribution system for movement of ozone within the apparatus.⁸ This results in disinfection and deodorization of objects placed within the apparatus.⁸

In-line treatment of hydrocarbons is accomplished by the use of ozone.⁹ Drill fluids contaminated by application of heat to vaporize contaminants are deodorized by ozonation.⁹

Water treatment plant on Huangpu river in China, equipped with coagulation, sedimentation, ozonation, biological activated carbon filtration, sand filtration, and chlorination in succession, was evaluated for ozonation capability of removal of multiple odorants.¹⁰ The process was effective in the simultaneous removal of the musty odor, (geosmin and 2-methylisoborneol) and the septic odor (bis(2-chloroisopropyl) ether, dimethyl disulfide, and diethyl disulfide).¹⁰ Complete removal of the septic odor needs further treatment by sand filtration and chlorination.¹⁰

Pre-ozonation led to the formation of carbonyl compounds at concentrations of 67.3 ± 43.3 $\mu\text{g/l}$ as the sum of 14 carbonyl compounds.¹¹ The dominant compounds were formaldehyde, acetaldehyde, glyoxal and methyl glyoxal contributing to 65% of total carbonyl content.¹¹ Coagulation/flocculation and sand filtration significantly removed (64–80%) the carbonyl compounds formed at the pre-ozonation step.¹¹

Conventional wastewater treatment plants are ineffective in removing a broad range of micropollutants, such as pharmaceuticals, X-ray contrast media, industrial chemicals, and their transformation products.¹² Out of 30 micropollutants studied, 11 micropollutants could still be detected after ozonation, but most of these were eliminated in subsequent granular activated carbon filtration.¹²

11.2 OXIDATION

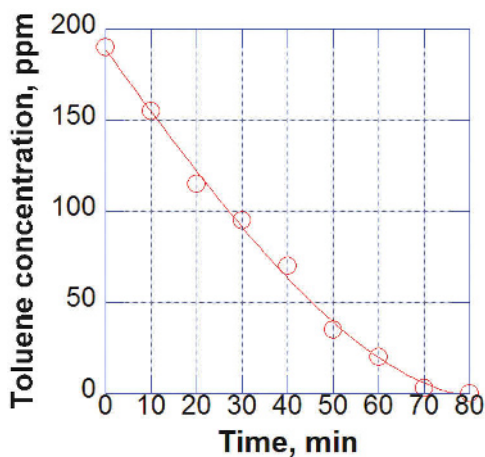


Figure 11.2. Toluene concentration vs. treatment time. Initial toluene concentration: 186 ppm. [Data from Somekawa S, Hagiwara T, Fujii K, Kojima M, Shinoda T, Takanabe K, Domen K, *Appl. Catalysis A: General*, 409–410, 209–14, 2011.]

Aqueous H_2O_2 decomposes over heterogeneous catalyst including metals, such as Fe, Cu, Pt, Ti, and Ni and metal oxides immobilized on various support materials such as sand, silica, zeolites and alumina.³ The decomposition of peroxide results in the formation of strong oxidants including $\cdot\text{OH}$ -radicals.³ The electrochemical mineralization of organic compounds is used for the disinfection of drinking water or treatment of wastewaters.³ Electrochemical oxidation mechanism involves the production of $\cdot\text{OH}$ -radicals at the active sites of the anode.³

Volatile organic compounds present at ppm levels were decomposed over the catalyst $\text{CuO}-\text{Co}_3\text{O}_4-\text{CeO}_2$ (Cu:Co:Ce = 10:45:45 mol%) for industrial odor control.¹³ Toluene was used as a VOC model compound and kinetic analysis of the total oxidation to carbon dioxide was conducted.¹³ The odor emitted from paint-drying processes can also be eliminated effectively using the above catalyst system.¹³ Figure 11.2 shows the toluene concentration vs. treatment time.¹³ It is quite apparent that oxidation is a substantially slower process than ozonation (compare with data in Figure 11.1).¹³ The desorption of products is thought to be rate-limiting; the interaction between the surface and products must be weakened for improved catalytic performance.¹³

Chemical oxidation was used for removal of hydrogen sulfide during treatment in an aerated biofilter.¹⁴ Biodegradation and oxidation were the two main removal mechanisms in the biofilter, whereas stripping and volatilization made only minor contributions.¹⁴

Inorganic peroxides, such as CaO_2 and MgO_2 were used for removal of odor from sediments and solid bodies, such as tablets, flakes, granules, briquettes, and prills.¹⁵ The invention is also directed to treating ponds, streams, canals, lagoons, etc.¹⁵

Dimethyl sulfide could easily be oxidized to dimethyl sulfone with neutral to alkaline hypochlorite solution containing stoichiometrically available chlorine.¹⁶

Indolic compounds are among the most smelly nitrogenous heterocyclic compounds identified in wastewaters, associated with livestock production.¹⁷ Indole has an unpleasant odor, and it may also cause acute pulmonary edema, emphysema, hemoglobinuria, and hemolysis.¹⁷ Iron-alginate beads were successfully applied as heterogeneous Fenton catalysts for the removal of a malodorous indole.¹⁷ Four reaction intermediates (isatin, dioxindole, oxindole and anthranilic acid) were identified.¹⁷

An odor control composition may be dosed to a wastewater treatment system to control hydrogen sulfide levels.¹⁸ The composition may include a sulfide-reducing agent and an oxidizer.¹⁸ The sulfide-reducing agent contains calcium nitrate, and sodium chlorite is an oxidizer.¹⁸

11.3 MICROOXYGENATION

Microoxygenation is widely applied for the maturation of red wines as an alternative to barrel aging.¹⁹ The improvements in wine quality include color stabilization, removal of unwanted off-odors, and improvements in wine mouth-feel.¹⁹ These aspects of red wine maturation can be linked to changes in polyphenol content, particularly involving the anthocyanins that give red wine its color, and flavanol oligomers and polymers associated with astringency.¹⁹

The generation of oxygen microbubbles from a porous diffuser (microbullage) is the most widely used technique in commercial applications, with several systems and units currently available.¹⁹ An alternative means of introducing oxygen into a fluid, besides the supply of O_2 bubbles, is through a permeable membrane, such as a plastic tube or vessel.¹⁹

Wine oxidation has also been associated with the formation of unwanted aromas, including 3-(methylthio)propionaldehyde with a “farm-feed” descriptor, phenylacetaldehyde described as “honey-like,” 1,1,6-trimethyl-1,2-dihydronaphthalene with a “kerosene” odor, and 4,5-dimethyl-3-hydroxy-2(5-H)-furanone.¹⁹ A number of these aldehydes were found at higher concentrations in aged than in younger red wines.¹⁹ The increase in dissolved oxygen in wines undergoing microoxygenation is meant to remain low, with the aim of ensuring that the wine will take up the oxygen without O_2 reaching higher levels where negative impacts may result.¹⁹ The increase in aldehydes leading to oxidized characters in wines is caused by high O_2 dosages or prolonged microoxygenation.¹⁹

The impact of microoxygenation and wood type present on wine maturation was studied.²⁰ For example, higher concentrations of furanic compounds were obtained with blends richer in French oak combined with high oxygen doses, or blends richer in American oak combined with low oxygen resulted in high toasting degrees.²⁰ The sensory analysis of wines showed differences in vanilla, woody, coconut, spicy, and chocolate attributes.²⁰

Treatment with microoxygenation accelerated the changes taking place in cider distillates when compared to traditional aging in barrels.²¹ The higher degree of oxidation in microoxygenated brandies was achieved, favoring the contents of benzoic derivatives and total acetaldehyde.²¹ Microoxygenated spirits showed a higher degree of hydrolysis, resulting in a higher concentration of oak lactones and gallic acid and a more pronounced decrease in the levels of 3-methyl-1-butyl acetate and 2-phenylethyl acetate.²¹

An electronic nose and an electronic tongue have been used to analyze red wines with high and low phenolic contents, and processed with or without microoxygenation.²² Combination of the electronic nose and the electronic tongue gave good correlations with parameters associated with the oxygen levels.²²

11.4 COMPLEX FORMATION

α -Lipoic acid is an essential cofactor in mitochondrial multi-enzyme complexes related to energy production.²³ However, it is unstable under light or heat, and its decomposition is accompanied by an unpleasant odor.²³ It can be stabilized by formation of a complex with chitosan.²³

The undesirable odor of paper hand towels is reduced by formation of an ester complex with carboxylic acid groups and hemicellulose present in papermaking fibers.²⁴ This ester complex formation neutralizes and eliminates free carboxylic acid groups in the tissue web that would normally take part in the generation of odorous compounds during drying.²⁴

There is a superabsorbent composition with tannins for odor control.²⁵ Combined use of hydrolyzable tannins and complex formation agents improves odor-binding properties.²⁵ Preferred complex formation agents include aminopolycarboxylic acids.²⁵ They are added in a concentration of 0.05 to 0.5 wt%.²⁵

Inclusion complexes of estragole (the main component of basil and tarragon essential oils) with α -cyclodextrin, β -cyclodextrin, and their derivatives were studied.²⁶ It was confirmed that the encapsulation of estragole with cyclodextrin is an efficient tool to improve its use in aromatherapy, cosmetics, and food fields.²⁶

11.5 COAGULATION

Natural organic matter is removed by coagulation during drinking water treatment.²⁷ The presence of natural organic matter causes many problems in drinking water and drinking water treatment processes, such as²⁷

- color, taste, and odor problems
- increased coagulant and disinfectant requirement (increased sludge volumes and production of harmful disinfection by-products)
- increased biological growth in distribution system
- increased levels of complexed heavy metals and adsorbed organic pollutants.

Natural organic matter can be removed from drinking water by several treatment options, of which the most common and economically feasible processes are coagulation and flocculation, followed by sedimentation/flotation and sand filtration.²⁷

Figure 11.3 shows the mechanism of organic matter removal by coagulation.²⁷ The aggregation mechanisms through which natural organic matter is removed include a com-

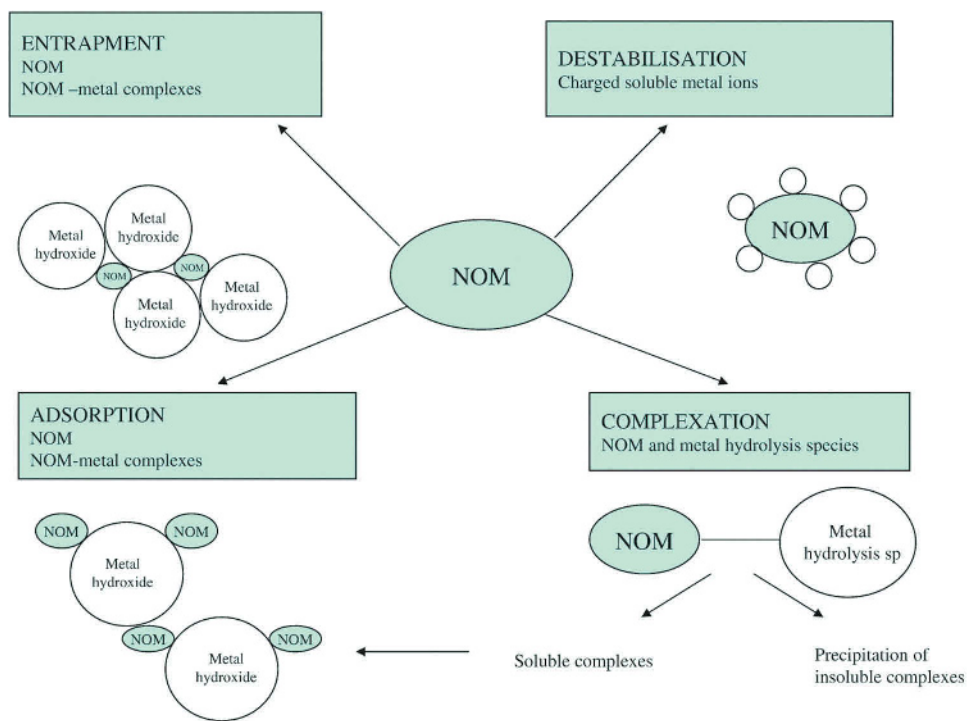


Figure 11.3. Removal mechanisms of natural organic matter, NOM, during coagulation. [Adapted, by permission, from Matilainen A, Vepsäläinen M, Sillanpää M, *Adv. Colloid Interface Sci.*, **159**, 189-97, 2010.]

bination of charge neutralization, entrapment, adsorption and complexation with coagulant metal ions into insoluble particulate aggregates.²⁷ The effectiveness of coagulation to remove natural organic matter and particles depends on several factors, including coagulant type and dosage, mixing conditions, pH, temperature, particle and natural organic matter properties (such as size, functionality, charge and hydrophobicity), as well as the presence of divalent cations and concentrations of destabilizing anions (bicarbonate, chloride, and sulfate).²⁷ More details about the coagulation processes and chemicals used can be found elsewhere.²⁷

Taste and odor are the primary indicators of the safety and acceptability of drinking water and their changes are mainly caused by the presence of two semi-volatile compounds – 2-methylisoborneol and geosmin.²⁸ Conventional treatment processes, such as coagulation, sedimentation and chlorination have been found to be ineffective for removal of 2-methylisoborneol/geosmin.²⁸ Studies have shown that powdered activated carbon, ozonation, and biofiltration are the most effective in removal of these two compounds.²⁸

The treatment of paint manufacturing wastewater by coagulation (aluminum sulfate) coupled to electrochemical methods was used to remove high coloration, turbidity, strong odor, and contain high loads of organic and toxic chemical substances such as surfactants, bactericides, oils, solvents, and preservative agents.²⁹ The chemical coagulation technique did not meet all the criteria for wastewater disposal, but water was sufficiently purified for reuse in paint production.²⁹

Further information on advancements in coagulation and its effect on natural organic matter removal can be found elsewhere.³⁰

11.6 DEGASIFICATION

The odor emissions of recycled polyolefins can be reduced by multiple degasifications during the extrusion process.³¹ The material is milled, water-cleaned, and then extruded in a double-screw-extruder with a vacuum unit.³¹ Multiple degasifications was applied by extruding the granulate up to four times.³¹ Threefold degasification of polyolefin leads to an odor reduction by 37%.³¹ After the fourth extrusion cycle, the odor concentration is increased.³¹ This is because degradation processes caused by the multiple thermal loading cause more harm than improvement in odor concentration.³¹

Effective degassing has multiple effects on products in the plastic and food industries.³² It reduces the residual moisture content, improves odor, changes visual appearance, affects mechanical properties, prevents bubbling or foaming, and homogenizes product.³²

Local overheating during extrusion can result in damage to the product such as changes in odor, color, chemical composition or the formation of inhomogeneities in the product such as gel particles or specks.³³ Degasification helps to reduce odor.³³

11.7 BIODEGRADATION

Hydrophobic, odorous VOCs, such as dimethyldisulfide, toluene or dimethylsulfide are often encountered in gaseous effluents from pulp and paper factories, composting facilities, food industries, and other industries.³⁴ Scrubbing using an organic solution (solvent) instead of an aqueous solution improves their removal.³⁴ Di-(2-ethylhexyl) adipate was selected as a solvent.³⁴ The kinetics of biodegradation in a two-phase partitioning system consisting of an emulsion of water and di-(2-ethylhexyl) adipate was studied.³⁴ Activated sludge was used as biodegradation culture.³⁴ Dimethyldisulfide and toluene biodegradation rates were 0.10 mg h^{-1} and 0.05 mg h^{-1} , respectively.³⁴ Unfortunately, di-(2-ethylhexyl) adipate was also degraded, which did not allow for the solvent to be reused in the process.³⁴

Antimicrobial polymer preservative (BactiBlock) has been developed to prevent deterioration, odors, corrosion, and stains in polymer-based products.³⁵ The additive is a very durable and cost-effective solution based on silver-functionalized clay.³⁵ It is designed to suppress the growth of algae, mold, mildew, fungi, and bacteria.³⁵ The silver linked to the clay platelets is released to the surface of the protected material at a controlled rate, ensuring a uniform and long-term antimicrobial effect.³⁵ Antimicrobial masterbatch (nShield) that inhibits the growth of odor-causing bacteria in synthetic fiber and plastic products has also been developed.³⁶ The additive offers easy processing and long-lasting effectiveness at low levels against a wide range of microorganisms in a variety of applications, including apparel, filtration, synthetic turf, automotive interiors, and variety of molding applications.³⁶ The antimicrobial agent's high thermal stability will not cause decomposition at polyamide-6, polyamide-6,6 or PET at their spinning temperatures.³⁶

Volatile organic compounds and odorous compounds create ecological and health hazards.³⁷ Biological waste air treatment processes using bioreactors have gained popularity in control of VOCs and odor.³⁷ A publication provides an overview of the various bio-

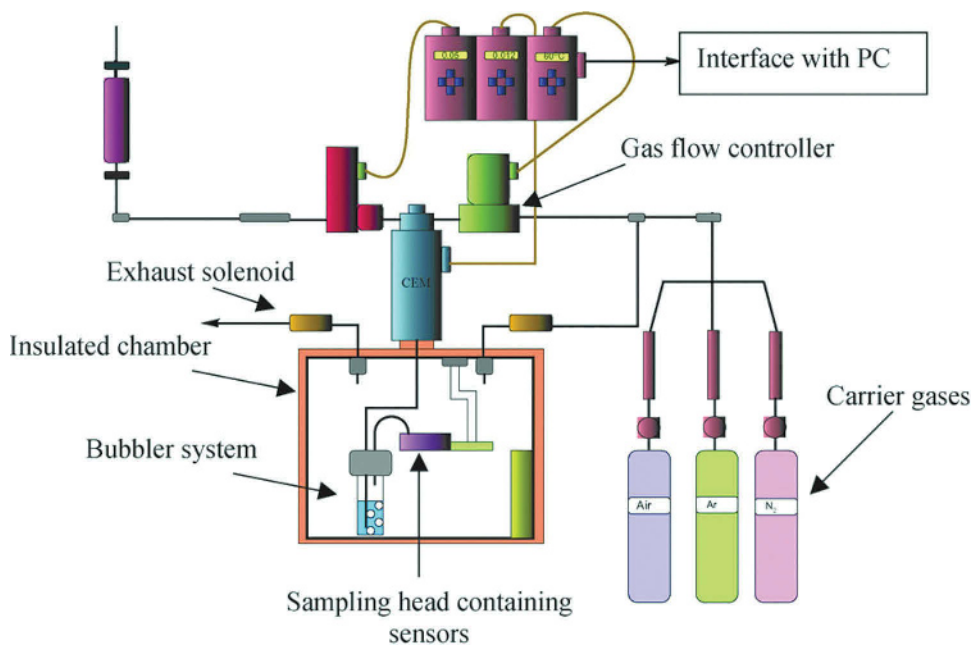


Figure 11.4. Testing apparatus of gases from the bacterial spoilage to be analyzed by the sensor system.

[Adapted, by permission, from Arshak K, Adley C, Moore E, Cuniffe C, Campion M, Harris J, *Sensors Actuators*, **B126**, 226-31, 2007.]

reactors that are used in VOC and odor abatement, details of their configuration and design, mechanism of operation, insights into the microbial biodegradation process.³⁷

Biodegradation of geosmin by a Gram-negative bacterium, Geo48, a member of the *Alphaproteobacteria* and similar to *Sphingopyxis alaskensis* was studied.³⁸ Initial geosmin concentrations ranging from 100 to 1000 ng/l influenced geosmin degradation, with rate constants increasing from 0.010 h⁻¹ to 0.029 h⁻¹, respectively.³⁸ Water temperature also influenced degradation of geosmin.³⁸

Biological sand filtration was an effective process for the complete removal of 2-methylisoborneol and geosmin.³⁹ Removal was predominantly through biodegradation.³⁹ The biodegradation of 2-methylisoborneol and geosmin was a pseudo-first-order reaction with rate constants ranging from 0.10 to 0.58 d⁻¹.³⁹ Rate constants depended on the initial concentration of the microbial inoculum, but not on the initial concentration of 2-methylisoborneol and geosmin.³⁹

Conducting polymer nanocomposite sensors are useful in real-time analysis and quantification of the odors produced by food-borne pathogens including *Salmonella* spp., *Bacillus cereus*, and *Vibrio parahaemolyticus*.⁴⁰ These microorganisms are three major food spoilage organisms.⁴⁰ Figure 11.4 shows experimental setup used in the analysis of odorous gasses from food spoilage caused by biodegradation.⁴⁰ The bacteria can be identified from the response pattern produced by the four sensors.⁴⁰

A filter plug for cigarettes, made out of cellulose acetate, has improved biodegradability and suppressed generation of acetic acid odor.⁴¹ The acetic acid odor can be sup-

pressed by the use of one of the following substances: 2-pyrrolidone, N-methyl-2-pyrrolidone, 2-oxazolidone, 3-methyl-2-oxazolidone, phthalimide, succinimide, riboflavin, pyrazine, and many others.⁴¹

A method for removing hydrogen sulfide from biodegradation products of animal waste has been patented.⁴² Sonication treatment of wastes has many important benefits, including a dramatic reduction of hydrogen sulfide emission, decrease ammonia emission, a decrease in odor, and an increase of biodegradation rate.⁴²

Gordonia sihwensis can sequester and biodegrade hydrocarbons.⁴³ It can be used for remediation of drill cuttings coated with drilling fluid and soil or sludges contaminated with oil contaminants.⁴³ Crude oil biodegradation completion was indicated by the lack of oil presence and no odor of crude oil remaining in the flask.⁴³ Complete biodegradation took 6 hours.⁴³

An integrated bioremediation process for petroleum hydrocarbons removal and odor mitigation from contaminated marine sediment has been developed.⁴⁴ In the first phase, acetate was dosed into the sediment as co-substrate to facilitate the sulfate reduction process in the presence of *Desulfobacterales* and *Desulfuromonadales*.⁴⁴ In the second phase, NO_3^- was injected into the sediment as an electron acceptor to facilitate the denitrification process in the presence of *Thioalkalivibrio sulfidophilus*, *Thiohalomonas nitratreducens* and *Sulfurimonas denitrificans*.⁴⁴

A method of inhibiting or preventing the production of laundry malodor caused by malodor-causing bacteria, such as *Bacillus subtilis*, *Bacillus amyloliquefaciens*, *Bacillus pumilus*, *Bacillus licheniformis*, *Bacillus atrophaeus*, and many other microorganisms.⁴⁵ The invention provides methods and composition for inhibiting malodor in a cleaning machine with microorganisms which are able to inhibit malodor caused by a malodor-causing microorganism (e.g., bacteria) present in the cleaning machine.⁴⁵

11.8 MICROORGANISM ENZYME

Concentrations of ammonia, hydrogen sulfide, and methyl mercaptan are high in the air above landfills in Taiwan.⁴⁶ Natural Effective Microorganisms Enzyme, NEME, was sprayed on selected sampling sites to reduce the odor.⁴⁶ In Tian-Wai-Tian Landfill in Ji-Long City, after NEME was sprayed, the odor reduction ratio was 99.4%.⁴⁶ In other landfill sites, the odor reduction ratio was from 62.1 to 72.2%.⁴⁶

The immobilized digestive lipase from Chinook salmon (*Oncorhynchus tshawytscha*), immobilized on a hydrophobic resin, was used to generate flavor compounds in milk.⁴⁷ It has potential application in developing dairy products with unique flavors.⁴⁷ Lipase are also proposed for use in laundry detergents.⁴⁹ Lipase and protease from *Aspergillus oryzae* is used for neutralization of pet litter odor.⁵⁰

A sanitary article includes a dried polymeric matrix with embedded enzyme.⁴⁸ The enzyme allows the sanitary article to absorb a bodily discharge fluid thereby the embedded enzyme functions in the production of antibacterial compounds or direct reduction of viable bacteria in the discharge fluid.⁴⁸ The enzyme activity promotes reduced odor in the sanitary article.⁴⁸ The enzyme used is a glucose oxidase or hydrolase.⁴⁸

11.9 BIOFILTRATION

The capacity of biofilter systems to remove volatile organic compounds in the presence of high concentrations of hydrogen sulfide was investigated for applications in the wastewater stations.⁵¹ The unit was composed of a biotrickling filter coupled with a biofilter.⁵¹ The biofilter media were plastic hollow spherical balls filled with a compost mixture, and the biotrickling filter media was a structured plastic packing.⁵¹ No inhibition effect was detected from the simultaneous biological removal of VOCs and H₂S.⁵¹ A traditional open in-ground biofilter filled with wood chips and compost, existing on the site, attained similar removal efficiencies for toluene, but the elimination capacity of the biotrickling/biofilter system was 3.3-times higher than the open biofilter.⁵¹

Biological techniques present lower operating costs (up to 6 times) and lower sensitivity than physical/chemical techniques.⁵² The biological technologies showed the lowest sensitivity and operating costs, biotrickling filtration exhibiting the lowest among them.⁵²

The performance and microbiology of a biotrickling filter treating methyl mercaptan, toluene, α -pinene, and hexane at the mg m⁻³ level was studied.⁵³ Removal efficiencies higher than 95% were recorded for MeSH, toluene, and α -pinene at 11 s, while hexane removal efficiency exceeded 70%.⁵³ The main phyla were *Proteobacteria*, *Actinobacteria*, *Nitrospira*, *Chloroflexi*, and *Gemmatimonadetes*.⁵³ Figure 11.5 shows schematic representation of experimental set-up.⁵³ Activated sludge was used in the biotrickling filter.⁵³

The deodorization performance of a biofilter and an activated sludge diffusion system was comparatively evaluated in terms of removal efficiency.⁵⁴ Removal efficiency for both systems was >95%.⁵⁴ A complete VOC removal can be expected in aerated tanks with fine bubble diffusers in water treatment plants under typical operational conditions.⁵⁴

MeOH removal efficiency, microbial ecology, and odor removal were studied.⁵⁵ The reactor was packed with wood bark chips without and with pH control (neutral).⁵⁵ The system operated at 96 g MeOH m⁻³ h⁻¹, achieving removal efficiencies of around 90% during the first stage and 99.9% during the second stage.⁵⁵ *Candida boidinii* was the most abundant microorganism in the first stage, and *Desulfovibrio*, *Desulfobacteraceae* species, *Methanosarcina* were the most abundant at the second stage.⁵⁵

A compost biofilter was established for the treatment of odors from biostabilization processing of municipal solid waste.⁵⁶ The compost biofilter had remarkable removal ability for alkylated benzenes (>80%), but poor removal for terpenes (30%).⁵⁶ Total VOC removal efficiency was from 20 to 95%.⁵⁶ The following microorganisms are responsible for odor removal: *Paracoccus denitrificans*, *Aminobacter aminovorans*, *Bacillus subtilis*, *Pseudomonas putida*, and *Exophiala*.⁵⁶

A modular biofiltration support is quickly erectable to any size and shape using plastic modules that are interconnected at the site.^{57,58}

Downflow biofiltration of hydrogen sulfide-containing gas has been developed.⁵⁹ The system is comprised of the biofilter, odor source process tanks, inlet piping, discharge piping, downstream biofilter.⁵⁹ Odorous gasses dissolve in a biofilm and microbes in the biofilm absorb and metabolize the odorous compounds, converting them into dissolved mineral products of decomposition.⁵⁹ Ground wood is advantageous as a packing material because it has high porosity and its organic content is readily colonized by microorganisms.⁵⁹

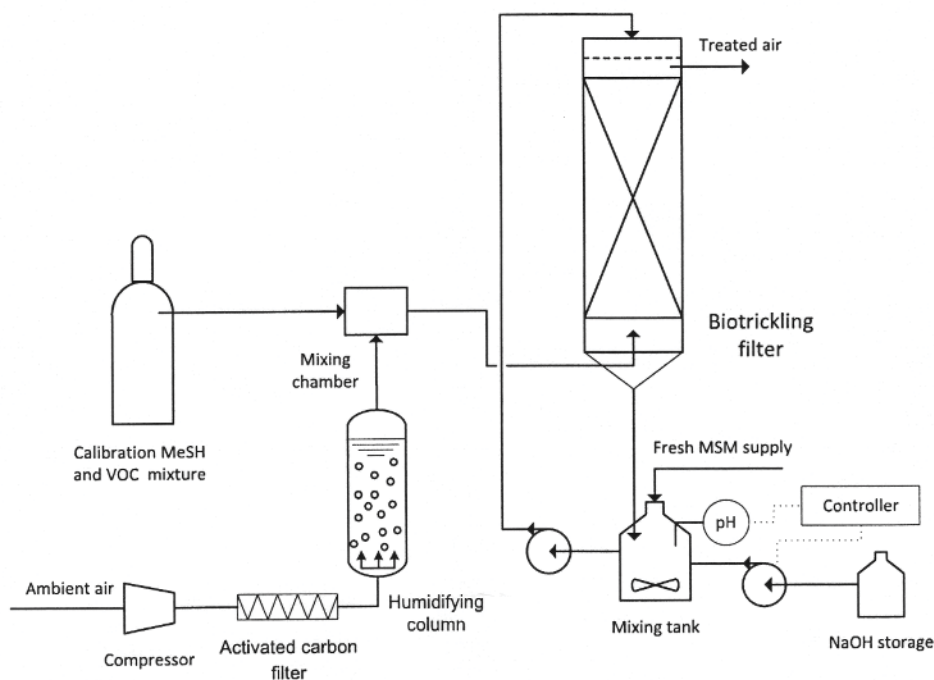


Figure 11.5. Schematic diagram of experimental set-up using biotrickling filter. [Adapted, by permission, from Lebrero R, Rodríguez E, Estrada J M, García-Encina P A, Muñoz R, *Bioresource Technol.*, **109**, 38-45, 2012.]

A biological filter contains grains having a hydrophilic nucleus and a hydrophobic coating.⁶⁰ The hydrophobic coating includes microorganisms and a metallic agent that both assist in the efficient breakdown of hydrogen sulfide.⁶⁰ Biofiltration is one of the most efficient odor contaminant removal technologies.⁶⁰ It is effective, economical, and environmentally friendly process when applied to dilute and biodegradable compounds.⁶⁰ The microorganisms include *Thiobacillus thioparus*, *beggiatoa*, *thiothrix*, and *feroxidans*.⁶⁰ The metallic agent is iron in a powder form.⁶⁰ Hydrophobic agent is clinoptilolite, activated carbon, or their combination.⁶⁰

A layer of particulate rubber is used as a filtration medium for use in treating contaminated gasses.⁶¹ The source of rubber is recycled tires.⁶¹ Eighty percent odor reduction was achieved after 6 weeks using a 1-inch thick layer.⁶¹

A biofilter medium to remove odor causing compounds from waste gas streams has a coating to support microorganisms.⁶² The core of the biofilter medium is an expanded glass.⁶² The coating may include a bonding agent, adsorptive agent, and nutrients for microorganisms.⁶² The bonding agent may be cement.⁶² The adsorptive agent may be activated carbon.⁶² The microorganisms include *Pseudomonas pseudoalcaligenes*, *Paenibacillus lautus*, *Thiobacillus thioparus*, and *Thiobacillus thiooxidans*.⁶² The nutrients may include phosphorus, nitrogen, potassium, and zinc acetate.⁶² The coating may include phosphoric acid.⁶²

One biofiltration system for odor control is a corrosion resistant gas treatment system.⁶³ It contains a housing divided into two sections connected by a gas passage.⁶³ Simultaneous remediation of contaminants from many contaminated gas streams is possible.⁶³ Moisture level, pH, and microorganism profiles for the two sections can be optimized for the target pollutants in the gas stream.⁶³ The contaminated air passes over organisms which convert the pollutants into innocuous compounds, thus removing odor and other undesirable compounds.⁶³

A submerged biofiltration purifying apparatus includes settling zone, filtering zones, and bubble aeration units connected to the bottom of filtration zones.⁶⁴ Soft contact media allow microorganisms to grow.⁶⁴ The bubble aeration unit generates bubbles that guide sewage flow towards soft contact media so that organic substances in the sewage are adsorbed to biological film.⁶⁴

A biofiltration applicator for controlling and accessing the initial point of contact is used in woodchip-based biofiltration system for odor and particulate matter removal from exhaust fan emissions from the animal feeding operation buildings.⁶⁵

The air cleaning device had straight and wavy plates.⁶⁶ The spaces (4 ± 0.2 mm) between the plates reduced the device's aerodynamic resistance.⁶⁶ The odor reduction was 5 to 10% greater when a wavy structure was used.⁶⁶

The life cycle assessment was performed to compare two biological treatments, namely biofilter and biotrickling filter, two physical/chemical alternatives, namely activated carbon tower and chemical scrubber, and a hybrid combination of biotrickling filter + activated carbon tower.⁶⁷ The frequent replacement of packing material in activated carbon tower was responsible for the highest environmental impact.⁶⁷ The hybrid technology was less recommendable than biofilter and biotrickling filter, but friendlier to the environment than physical/chemical treatments.⁶⁷

The durability and effectiveness of a biofilter for waste containers is improved by the addition of heat- and drought-tolerant microorganisms.⁶⁸ Different spore-forming *Bacillus* isolates ensure a satisfactory odor reduction even at the extreme living conditions (heat, cold, drought) in a biofilter cover and at long storage life of the filter material.⁶⁸

Purification of a microbiological biogas from the methane fermentation aims at removal of contaminants, particularly H_2S , under anoxic conditions, in an installation containing a biofilter loaded with a biological filter bed sprinkled with a mineral medium (nitrogenous salts of alkali metals of the I and II group), containing immobilised microorganisms (*Thiobacillus denitrificans*) capable of degrading sulfur compounds.⁶⁹

11.10 PHOTOCATALYSIS

UV-photolysis is widely used for disinfection purposes.³ It involves the interaction of artificial or natural radiation with the target molecules and compounds, causing a series of photochemical reactions.³ The effect of photolysis depends on absorption of the emitted radiation by target molecules.³ Observable effects only occur when high irradiation doses are applied.³ Under vacuum UV radiation, water molecules dissociate into hydrogen atoms, hydroxyl radicals, and hydrated electrons.³ Vacuum UV oxidation is efficient in natural organic matter reduction.³ Application of UV and, in particular, VUV causes the formation of undesired by-products, such as nitrite, which is regulated by EU (max. conc.

0.5 mg L^{-1}).³ Nitrite formation in natural water has not been observed in all cases.³ Its concentration significantly decreases when VUV radiation of 25 J cm^{-2} is applied.³

The photocatalytic and antibacterial activities of TiO_2 films on PVC were evaluated by monitoring the photodecomposition of 2-(phosphonomethylamino) acetic acid, methylene blue, and *Micrococcus lutes* (odor causing bacteria).⁷⁰ Successive-ionic-layer-adsorption-and-reaction deposition technique was used to deposit TiO_2 films on poly(vinyl chloride) and glass substrates.⁷⁰ Highly reactive hydroxyl radicals, which oxidize organic matter, could be created by using TiO_2 in the presence of water and oxygen under UV irradiation.⁷⁰ 2-(Phosphonomethylamino) acetic acid was completely degraded by UV solar simulator radiation on exposure over TiO_2/PVC film for 100 min (90% remained when TiO_2 was not present during UV exposure).⁷⁰ All colonies of *Micrococcus lutes* were destroyed by UV solar simulator radiation on exposure over TiO_2/PVC film for 20 min (85% colonies remained when TiO_2 was not present during UV exposure).⁷⁰

Photocatalytic activity of TiO_2 in a scrubber system for odor control, using methyl mercaptan gas as a target compound, was investigated.⁷¹ Removal of methyl mercaptan present in air has become urgent for improving health requirements because of its release from wood-pulping industry, sewage treatment works, and petroleum-refining processes in urban cities like Hong Kong.⁷¹ Increased water pH facilitated absorption of methyl mercaptan in water (four times higher absorption than in acidic or neutral water).⁷¹ In basic TiO_2 suspensions, 96.3% of dissolved methyl mercaptan was degraded with pseudo-first-order kinetic constant being roughly 1.5 and 2.7 times of constants in neutral and acidic TiO_2 suspensions, respectively.⁷¹ Figure 11.6 shows the experimental set-up of a photocatalytic scrubber system.⁷¹ Addition of TiO_2 into the scrubber system can greatly improve the treatment efficiency of the reactor in removing odorous gases and particularly methyl mercaptan.⁷¹

Photocatalytic materials used to degrade organic and inorganic pollutants now include, in addition to TiO_2 , ZnO , Fe_2O_3 , WO_3 , MoS_2 , and CdS . Nanoparticles' unique properties, such as surface to volume ratio and quantum effects, improve the efficiency of photocatalysis in environmental remediation, odor control, and sterilization.⁷² Figure 11.7 shows the mechanism of photocatalysis. The lifetime of an electron-hole pair ($e^- h^+$ pair) is a few nanoseconds, sufficiently long to produce redox reactions in the solution or gas in contact with the photocatalyst.⁷² The hole oxidizes water to hydroxyl radicals and the electron gives itself to an acceptor molecule.⁷² This leads to a chain of photochemical reactions. More information on photocatalysis can be found elsewhere.⁷²

Oxidation of air contaminants is enhanced by the ultralow density of a UV-accessible aerogel catalyst.⁷³ A catalyst bed is formed of a titanium dioxide aerogel. A high fraction of the titanium dioxide aerogel is accessible to UV light and gas.⁷³ The catalyst bed is exposed to UV radiation from a UV source and a stream of contaminated gas is introduced into the photocatalytic reactor cell.⁷³ Anatase titanium dioxide is then the most frequently used photocatalyst.⁷³ Electron holes produced in the photochemical reaction are very powerful oxidizing agents.⁷³ Their oxidation potential is sufficient for a complete oxidation of nearly any compound.⁷³ In the presence of air or oxygen, UV-irradiated titanium dioxide is capable of total destruction of methane, ethane, toluene, carbon monoxide, acetone, butanol, xylene, formaldehyde, butyraldehyde, and odor compounds including acetaldehyde, isobutyric acid, toluene, methyl mercaptan, hydrogen sulfide, and trimethyl amine.⁷³

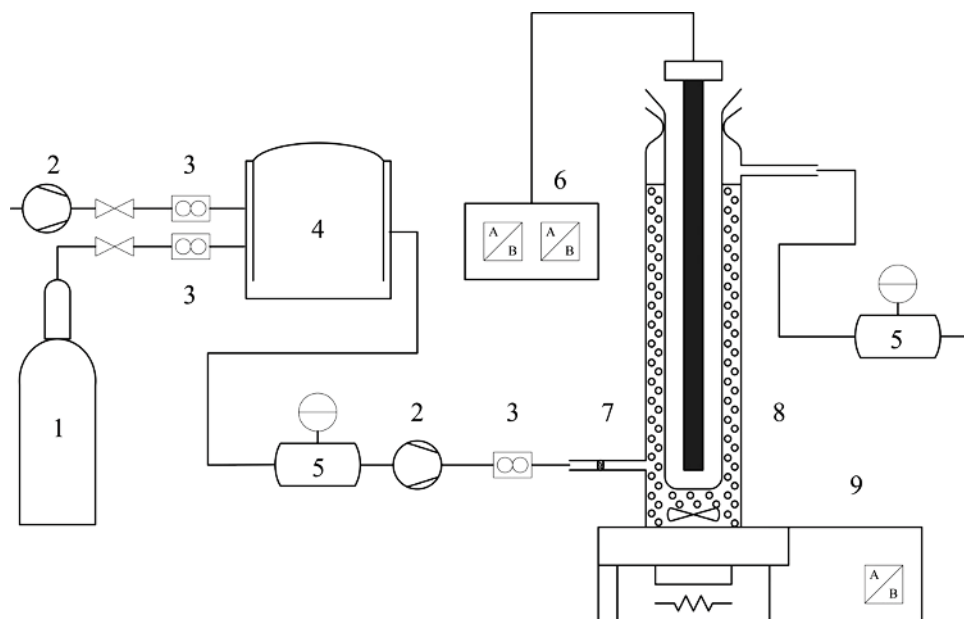


Figure 11.6. Schematic representation of the photocatalytic scrubber system for removing methyl mercaptan gas: 1 – methyl mercaptan gas cylinder, 2 – air pump, 3 – flow meter, 4 – gas bag, 5 – methyl mercaptan sensor, 6 – controller of UV lamp, 7 – sintered glass diffuser, 8 – photoreactor, 9 – magnetic stirrer. [Adapted, by permission, from La N, Tu H Y, Su Y, Wu Y, *Separation Purification Technol.*, **90**, 196-203, 2012.]

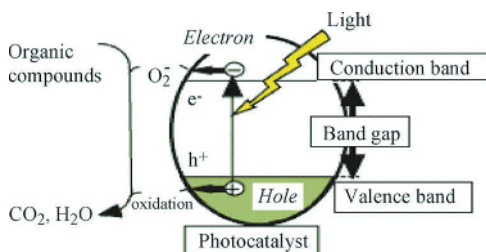


Figure 11.7. Mechanism of photocatalysis: this diagram shows formation of holes (h^+) and electrons (e^-) upon irradiation in the presence of catalyst. [Courtesy of TitanPE Technologies, Inc., Shanghai, PRC.]

In an aqueous medium, titanium dioxide photocatalyzed complete oxidation of phenol, chlorinated phenols, dioxins, polychlorinated biphenyl, DDT, surfactants, saturated aliphatic hydrocarbons, pesticides, and s-triazine.⁷³

In another solution, UV source irradiates a plurality of photocatalytic beads.⁷⁴ Enclosure permits air flow, accommodates the radiation source and the photocatalytic beads.⁷⁴ The apparatus is designed for decomposing odor-producing ingredients

at low temperature.⁷⁴ A low-pressure mercury lamp is used as a source.⁷⁴ The beads have a spherical body made of silica gel and the photocatalyst layer is made of titanium dioxide.⁷⁴ Silica gel can absorb moisture, which promotes photocatalysis.⁷⁴ Hydroxyl radicals are generated around the photocatalyst.⁷⁴ The process is conducted at 5°C to maintain the excited condition of the photocatalyst, which increases its effectiveness of odor removal and decomposition of odor ingredients.⁷⁴

Cold plasma, UV radiation, and photocatalyst are used in the treatment of gaseous effluents.⁷⁵ The invention is applicable in chemical, food, agricultural, and petrochemical industries, paint workshops for odor destruction.⁷⁵ Titanium dioxide is used as a catalyst.⁷⁵

Data shows that combination of plasma, UV, and catalyst increases the rate of degradation over the UV+catalyst combination.⁷⁵

A photocatalytic fog disseminating system is used to disperse and activate photocatalytic particles.⁷⁶ The photocatalytic particles are made of nano-titanium dioxide.⁷⁶ Particles are dispersed as an aerosol and a photon source is used to excite dispersed particles in order to initiate photocatalytic redox reactions that degrade airborne or sedentary organic impurities that come in contact with the aerosol.⁷⁶

Multifunction photocatalytic paint has two layers.⁷⁷ The first layer is a water-based suspension of insoluble calcium compound; the second (surface) layer is a mixture of nano-titanium dioxide suspended in water.⁷⁷ The multifunctional coatings possess the covering, cleaning, sanitary, antibacterial, antimold, photocatalytic, and other functionalities.⁷⁷ The insoluble calcium compound is calcium carbonate also in the nanosize range.⁷⁷

TiO₂ photocatalyzed elimination of 2-isopropyl-3-methoxy pyrazine taste and odor compound in aqueous phase.⁷⁸ Photogenerated hydroxyl radicals were responsible for degradation.⁷⁸

Photocatalytic deodorization was applied to the household appliances.⁷⁹ Titanium dioxide was used as a catalyst and radiation had a range of 380-400 nm.⁷⁹ Transparent photocatalytic coating for odor removal contains WO₃, TiO₂, or Ti(O,C,N)₂·Sn.⁸⁰ The co-catalyst is a metal oxide capable of being reduced by electron transfer from the conduction band of the photocatalyst.⁸⁰ The co-catalyst is a metal oxide capable of reducing O₂ by electron transfer to superoxide radical ion.⁸⁰

An air cleaning system uses a photocatalyst responsive to visible light, which can be regenerated after being contaminated during a photocatalytic reaction.⁸¹

11.11 ACTIVATED CARBON

When activated carbon is used, the natural organic matter is not only a target for adsorptive removal but also an inhibitory substance that reduces the removal efficiency of trace compounds, such as 2-methylisoborneol through absorption competition.⁸² Superfine (submicron-sized) activated carbon was developed by wet-milling of commercially available powdered activated carbon to a smaller particle size.⁸² The increased natural organic matter uptake by superfine activated carbon did not result in a decrease in 2-methylisoborneol adsorption capacity beyond that obtained as a result of natural organic matter adsorption by powdered active carbon (regular size).⁸²

The adsorption of the taste and odor compounds, such as geosmin and 2-methylisoborneol onto powdered activated carbon has been studied under conditions typical for a drinking water treatment plant that uses reservoir water for drinking water production.⁸³ The reservoir water contains natural organic matter which competes for absorption sites with odor compounds.⁸³ Different models were used to determine the dosage of activated carbon required to eliminate odors.⁸³

A standard carbon lifespan of 6 months is used in the case of an activated carbon filter.⁵² The cost and lifespan of the activated carbon are the main contributors to the overall operational costs (66%).⁵² Activated carbon adsorption is the most expensive technology in overall costs (as compared with biofilter, biotrickling filter, and chemical scrubber).⁵²

Five powdered activated carbons, including a fruit-based, a wood-based, and three bituminous coal-based, were selected to study the effects of surface characteristics of acti-

vated carbon on the adsorption of 2-methylisoborneol and geosmin.⁸⁴ All carbons showed a broad absorption band in the 1300–1000 cm^{-1} region, which can be assigned to C–O stretching and O–H bending modes of alcoholic, phenolic, and carboxylic groups.⁸⁴ The iodine number, methylene blue number, meso and total pore volumes, surface area, O and C–O contents were found to be insignificant in correlation with the adsorption capacities of 2-methylisoborneol and geosmin.⁸⁴ The volume of micropores is an effective indicator for the selection of activated carbon for the removal of both 2-methylisoborneol and geosmin.⁸⁴

The role of surface acidity and pore size distribution in the adsorption of 2-methylisoborneol *via* powdered activated carbon has been studied.⁸⁵ The pore size distributions and the percent removal of 2-methylisoborneol indicated that a range of micro- and mesopores (1.2–10 nm) were necessary regardless of natural organic matter concentration.⁸⁵ The performance of the activated carbon indicated that the surface chemistry did affect 2-methylisoborneol removal.⁸⁵

The effect of ozone on the adsorption characteristics of methyl ethyl ketone vapor on activated carbon was investigated.⁸⁶ The destruction of methyl ethyl ketone can be effectively promoted by the increase of the bed height of activated carbon and the increase in the concentration of ozone.⁸⁶ An adsorption process in combination with the ozone oxidation shows potential for the control of VOCs and odors.⁸⁶

Odor-sorbing packaging material is obtained by coating one side of flexible packaging with absorbing composition, which contains an effective concentration of activated carbon.⁸⁷ Substrate for the coating is LDPE film.⁸⁷ It is coated with an aqueous composition composed of binder and activated carbon.⁸⁷ Aqueous styrene acrylate emulsion is a suitable binder. Coating contains 50 wt% of activated carbon.⁸⁷

Activated carbon/metal oxide is used for odor control.⁸⁸ The filter element may be prepared by mixing activated carbon, metal oxide, and binder.⁸⁸ The filter element is useful in removal of odorous compounds, acidic gases, and volatile compounds from gases.⁸⁸ Any metal oxide that enhances the sorptive capacity of activated carbon may be used.⁸⁸ Preferred oxide is magnesium oxide.⁸⁸ Magnesium aluminosilicate is used as a binder.⁸⁸ The mixture may be extruded in a form of strand, ribbon, or pellet, and then calcinated at 300°C.⁸⁸ This filter element reduces concentration of hydrogen sulfide below the odor threshold level by catalytically oxidizing it to elemental sulfur or sulfuric acid.⁸⁸

Activated carbon with metal oxide matrix for odor control may be obtained by a method including the steps of preoxidizing a carbon material, grinding material with metal oxide to form carbon mixture, extruding carbon mixture, and carbonizing and activating the extrudate.⁸⁹ Magnesium oxide is used as a metal oxide.⁸⁹

Activated carbon, calcium carbonate, and binder form an odor-controlling composition.⁹⁰ The binder is nonionic cellulosic ether (e.g., methylcellulose, hydroxypropylmethyl cellulose, etc.). Calcium carbonate is used to change the color of the composition.⁹⁰

Encapsulation of activated carbon protects its structure and preserves its absorbing capabilities.⁹¹ Non-water soluble, amorphous polymer is used for encapsulation.⁹¹ Linear low density polyethylene is preferred polymer used in encapsulation.⁹¹ The loading of activated carbon is from 0.2 to 10 wt%.⁹¹

Activated carbon is used for removal of dimethyl sulfoxide.⁹² The system includes activated carbon filters, adsorbents, odor absorbing fabric, masks, clean air members, and

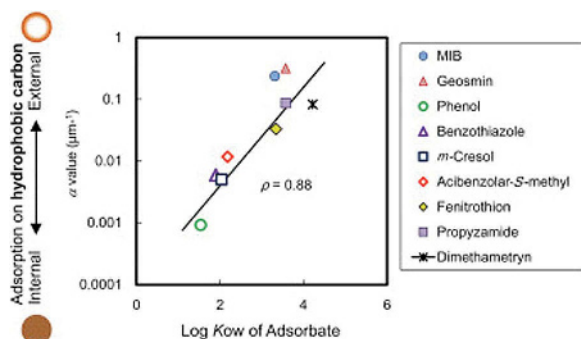


Figure 11.8. Correlation between α and K_{OW} for various adsorbates on activated carbon. [Adapted, by permission, from Matsui, Y; Nakao, S; Sakamoto, A; Taniguchi, T; Pan, L; Matsushita, T; Shirasaki, N, *Water Res.*, **85**, 95-102, 2015.]

a clean air supply assembly.⁹² Dimethyl sulfoxide is a highly promising therapeutic agent used for treatment of head injuries.⁹² Its drawback is undesired odor, which is reduced by the application of this system.⁹²

An apparatus for odor control uses panels of activated carbon cloth.⁹³ The activated carbon cloth comprises activated carbon fibers, which are woven or knitted as a part of synthetic material.⁹³ The cooking vapors and fumes are retained on the activated carbon cloth.⁹³

The dielectric barrier discharge regeneration process of an activated carbon saturated with dimethyl sulfide was studied on a laboratory scale.⁹⁴ A high regeneration efficiency (>90%) was achieved in successive regeneration cycles (10 cycles).⁹⁴

The homogenous surface diffusion model was applied to predict the appropriate powdered activated carbon doses for the removal of 2-methylisoborneol (2-MIB) in drinking water.⁹⁵ The predicted and observed results were within 10% range.⁹⁵

The adsorbate molecules do not completely penetrate the adsorbent particle, but they preferentially adsorb near the external surface of the particle.⁹⁶ When the carbon particle radius is substantially larger than the penetration distance, the interior region of the carbon particle is not used.⁹⁶ When the particle radius is much smaller than the adsorbate penetration distance, the adsorption capacity is independent of the particle size, and the chemistry of the pore surface is the main determinant of adsorption capacity.⁹⁶ The equilibrium adsorption capacity increases with decreasing carbon particle size until the particle radius becomes much smaller than the penetration distance.⁹⁶ The shell adsorption model quantitatively describes the adsorbent particle size dependence of adsorption capacity.⁹⁶ The adsorption capacity dependence observed for geosmin and 2-methylisoborneol was due to their hydrophobicity (K_{OW}) and other chemical properties such as molecular structure, which also contribute to the high α (the thickness of the penetration shell) values of geosmin and 2-methylisoborneol (Figure 11.8).⁹⁶

The encapsulated activated carbon is produced to protect the structure of the activated carbon and preserve the odor absorbing capability of the activated carbon particles.⁹⁷ When activated carbon is blended with a molten polymer (for example to produce the film) its porosity can be reduced due to the penetration of the polymer molecules into the activated carbon.⁹⁷ As a result, the odor absorbing capability of the activated carbon is reduced as compared to the original powdery state.⁹⁷ Polystyrene is the encapsulating polymer, which does not reduce the porosity of activated carbon and protects it during processing.⁹⁷

11.12 ABSCENTS

Abscent is a combination of zeolites, including (1:1) activated silicalite and zeolite LZ-10.⁹⁸ Abscent is a deodorizing powder.⁹⁸ It is used in products where odor is a problem.⁹⁸ This molecular sieve is highly selective in adsorbing odor-causing compounds like aldehydes and ketones.⁹⁸ Abscent is very effective in decreasing the odor of molecules. It has organophilic pores that trap odor molecules within its structure.⁹⁸ Abscent is different than other molecular sieves due to its capacity for adsorbing odor-causing compounds even in the presence of water.⁹⁸ One of the benefits of abscents is their ability to remove many odorous compounds below their threshold detection level.⁹⁸ In application to drinking water, abscent was added to HDPE pellets and effect of its amount was determined.⁹⁸ When the maximum amount of abscent was added (0.3 wt%), almost all the carbonyl compounds disappeared, and the intensity of odor decreased.⁹⁸

11.13 ADSORBENTS

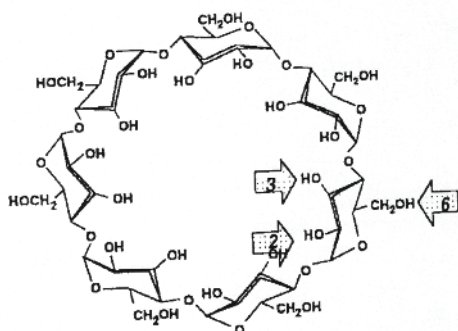


Figure 11.9. β -Cyclodextrin ($C_{42}H_{69}O_{40}$), the numbered arrows indicate the 2-, 3- and 6-position free hydroxyl groups on every glucopyranose unit in the cyclodextrin, which differ both in their functions and reactivity. [Adapted, by permission from Hirayama F, Uekama K, *Adv. Drug Delivery Rev.*, **36**, 125–41, 1999.]

Cyclodextrin/epichlorohydrin was synthesized and used as an adsorbent to remove two taste and odor-causing compounds, namely, 2-methylisoborneol and geosmin, from Lake Michigan water.⁹⁹ The current practice to alleviate the odor in the drinking water supply lines of the city of Chicago is to use powdered activated carbon at the intake of the water purification plants.⁹⁹ β -Cyclodextrin (Figure 11.9) was selected as a monomer because of its lowest water solubility (18.4 g/L) among the cyclodextrins and it was crosslinked with epichlorohydrin to form the adsorbent.¹⁰⁰ Cyclodextrins are byproducts of starch fermentation. They are used in the pharmaceutical industry for adsorption and time-release of drug substances.⁹⁹

Stable complexes between cyclodextrin and various chemicals are formed as a result of van der Waals forces, hydrogen bonding, and hydrophobic forces.⁹⁹ The complexes are formed in the apolar environment of the cyclodextrin cavity.⁹⁹ β -Cyclodextrin has an average cavity size of 5.2 Å with less inner cavity distortion as compared to other cyclodextrin monomers upon hydration.⁹⁹ β -Cyclodextrin crosslinked with epichlorohydrin is known for its adsorption of drugs, removal of bitterness from food products, and also as a stationary phase for liquid chromatography.⁹⁹ β -Cyclodextrin/epichlorohydrin copolymer has been used for removal of plasticizers and organic pollutants from the flowing water stream.⁹⁹ The synthesized polymer was made insoluble in water, so it would not leave any traces after treatment of lake water.⁹⁹ The results of studies confirmed that synthesized copolymer has potential use as an alternative to activated carbon.⁹⁹ It has advantage over activated carbon because it can be easily desorbed and reused.⁹⁹

Cyclodextrins and their derivatives are used to suppress unpleasant tastes and odors (e.g., debittering agents) or to achieve a controlled release of certain food constituents.¹⁰¹ Crosslinked, insoluble cyclodextrin polymer, water-soluble, cyclodextrin-grafted carboxymethylchitosan, and carboxymethylcellulose were used as debittering agents.¹⁰¹ The cyclodextrin polymers were obtained by the reaction of β -cyclodextrin with one of the following crosslinking agents: epichlorohydrin, diphenyl carbonate, or hexamethylene diisocyanate.¹⁰¹ Insoluble cyclodextrin polymer was obtained by reticulation under microwaves of propargyl- β -cyclodextrin with 1,3-bis(azidomethyl) benzene through Huisgen 1,3-dipolar cycloaddition.¹⁰¹ The crosslinked cyclodextrin polymers formed inclusion complexes with naringin.¹⁰¹ The soluble cyclodextrin polymers interacted with bitter flavonoids of citrus fruits (naringin and limonin).¹⁰¹ They thus behaved as bitter-masking agents.¹⁰¹

Chitosan microspheres prepared by a spray-drying process have a spherical geometry and a smooth surface morphology.¹⁰² Chitosan/cellulose blend beads were prepared *via* homogeneous dissolution of chitosan and cellulose in N-methylmorpholine-N-oxide.¹⁰² Chitosan/cellulose blend beads have potential applications in odor treatment as well as metal ions adsorption.¹⁰²

Aluminium oxide, zeolite, or activated charcoal were added in the extrusion process to adsorb the odorous substances from used oil bottles of HDPE.¹⁰³ Aluminum oxide did not change odor concentration, 20 wt% addition of zeolite reduced odorous substances by 46%, and 20 wt% addition of activated charcoal reduced odor concentration by 51%.¹⁰³

An odor-control system includes adsorbent material with a carrier structure.¹⁰⁴ Particles of adsorbent have a porous structure.¹⁰⁴ The pore structure has been configured in such a way that it can hold water and is inaccessible to odor-causing organisms.¹⁰⁴ Cellulosic and synthetic polymer fibers, and open-celled foams are used as carriers.¹⁰⁴ Adsorbent can be either inorganic or organic material.¹⁰⁴ Suitable inorganic materials include activated carbon, silicates, metal oxides, zeolites, carbonates, phosphates, borates, aerogels and their combinations.¹⁰⁴ Suitable organic materials include, for example, cellulosic materials, starches, chitins, alginates, synthetic polymers or their combinations.¹⁰⁴

Antimicrobial fibrous substrate contains a halogenated microbial agent and an odor adsorbent to reduce the level of odor usually associated with halogenated antimicrobial agents.¹⁰⁵ Heterocyclic N-halamine is a halogenated microbial agent, and adsorbent is selected from the group, including activated carbon, zeolites, silica, alumina, magnesia, titania, clay, and cyclodextrin.¹⁰⁵

Solid odor absorbers include a solid carrier with nanostructured surface and active zinc ricinoleate as an odor absorber.¹⁰⁶ Solid carriers are nanoporous anodically oxidized metals, namely titanium dioxide.¹⁰⁶ Odor absorber is combined with solubilizers and/or activators, such as anionic surfactants, aminoacids, especially arginine and lysine.¹⁰⁶ Additional odor-adsorbing agent such as cyclodextrin can also be added.¹⁰⁶

An evaporative pad contains a highly absorbent layer, which has non-absorbent material carrying a coating of absorbent particles bound to exposed surfaces of non-absorbent material.¹⁰⁷ Non-absorbent material can be a sheet of paper coated with plastic material.¹⁰⁷ The adsorbent particles are activated carbon, zeolite, synthetic molecular sieves, or their combinations.¹⁰⁷ These pads find application in humidifiers and evaporative coolers.¹⁰⁷

An odor-control substrate contains a plurality of fibers oriented in z-direction.¹⁰⁸ An odor control coating is applied to the substrate in such a manner that the majority of the coating is on the exposed side of the substrate.¹⁰⁸ Adsorbents used in the odor control coating include activated carbon, zeolites, silica, clays (e.g., smectite clay), alumina, magnesia, titania, cyclodextrin, and their combinations.¹⁰⁸

A pad for absorption of odors produced by humans contains activated carbon to absorb undesired masking-odors.¹⁰⁹

Humic acid causes the formation of odor in drinking water and reacts with chlorine to produce potential carcinogens such as trihalomethane and haloacetic acid during drinking water treatment.¹¹⁰ Zinc oxide-coated zeolite was developed by both nitric acid modification and $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ functionalization of zeolite 4A.¹¹⁰ ZnO-coated zeolite removes humic acid by a strong electrostatic interaction between the negative functional groups of humic acid and the positive charges on the ZnO-coated zeolite.¹¹⁰

The addition of adsorbent to the coagulation process is an emerging treatment solution for targeting hard-to-remove dissolved organic compounds from both drinking water and industrial wastewater.¹¹¹ Organoclay adsorbent with ferric chloride coagulant helped in removal of nearly all of the dissolved aromatics.¹¹¹

An odor adsorbent for use in absorptive hygiene articles comprises peroxomonosulfuric acid or its salt and zeolite.¹¹²

11.14 FILTERS

Polymer filters treated by plasma-assisted graft polymerization, nonthermal plasma, and their combinations are developed for use as multifunctional filters that can simultaneously remove odor and particulate.¹¹³ A nonthermal plasma-treated filter can adsorb a large amounts of ammonia but its performance deteriorates significantly after one month, whereas that of a plasma-assisted graft polymerization followed by nonthermal plasma-treated filter deteriorates only slightly.¹¹³ The particulate collection efficiency of a both-side plasma-assisted graft polymerization-treated filter is higher than that of an untreated filter, whereas that of the nonthermal plasma-treated filter is slightly lower.¹¹³ A high performance filter for removing odor and particles simultaneously can be obtained by the plasma-assisted graft polymerization treatment.¹¹³ Figure 11.10 shows the apparatus used for the plasma-assisted graft polymerization treatment.¹¹³ Plasma-assisted graft polymerization treatment is realized with acrylic acid monomer deposited only on one side of the filter.¹¹³ The apparatus can evenly irradiate radio frequency (RF=13.56 MHz) non-equilibrium plasma of a rare gas (a helium and argon mixture) on the surface of the filter by a parallel plate capacitively coupled plasma dielectric barrier nozzle electrode.¹¹³ The continuous exposure of the cloth to an acrylic acid mist is realized.¹¹³ The resulting chemical reactions cause polymerization of the cloth's fibers.¹¹³ A porous acid polymer layer, which can adsorb gaseous components, is produced on the filter surface.¹¹³ Unreacted monomer remaining on the filter surface is washed away with water and then dried completely.¹¹³ Both sides of the filter can undergo plasma-assisted graft polymerization; in this two-step process, one side of the filter would undergo treatment, followed by the other side.¹¹³

All plastic waste recycling plants in Taiwan used a filter to treat the melting fumes, and this did not efficiently eliminate the gaseous compounds and malodor.¹¹⁴

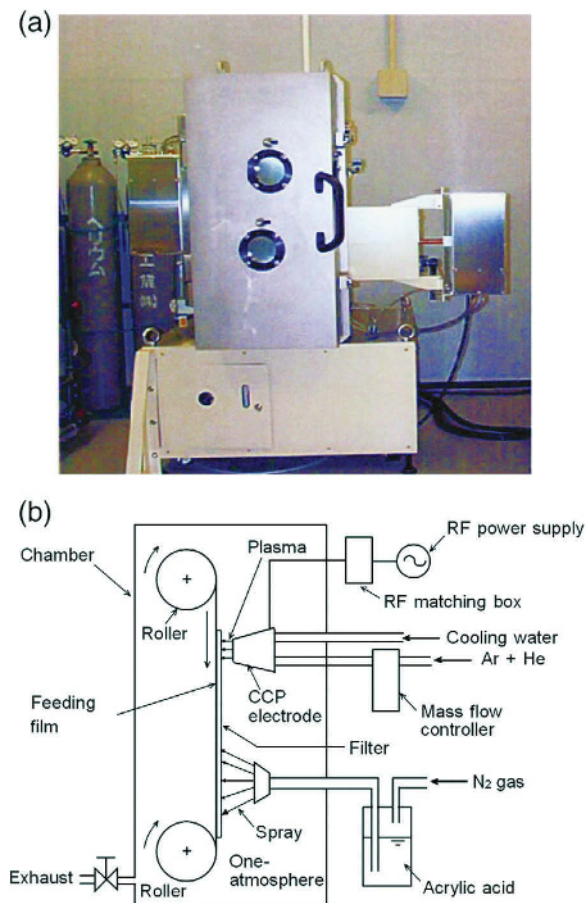


Figure 11.10. The experimental apparatus employed for plasma-assisted graft polymerization treatment: (a) overview and (b) schematic diagram. [Adapted, by permission, from Okubo M, Kuroki T, Saeki N, *Thin Solid Films*, **519**, 6994-98, 2011.]

Used supply air filters were studied by sensory and chemical methods.¹¹⁵ The prefilter was the main odor source in the ventilation unit, but when the humidifier was turned on, the odor was released mainly from the fine filter.¹¹⁵ Aldehydes, carboxylic acids, and nitrogen-containing organic compounds were the main emission products in the thermodesorption analyses of the filter dust.¹¹⁵ Many of these compounds have low odor threshold and, therefore, contribute to the odor released from the filters.¹¹⁵

Bacterial growth can harm filters through unwanted layers of biofilm, the addition of unwanted tastes and odors, and premature clogging.¹¹⁶ To remedy the problem of bacteria build-up and microbe growth in water filters and to address customer requests for filters with antimicrobial, a silver-based antimicrobial compound, provided by AgION Technologies, was used.¹¹⁶ The compound is comprised of silver ions and a zeolite.¹¹⁶ The silver reversibly binds to the zeolite, which has a unique property of releasing silver when exposed to

moisture, killing microbes that generally flourish in moist environments.¹¹⁶ Because the silver release is equilibrium-controlled, not dissolution-controlled, it maintains a low and consistent level of silver for the lifetime of the filter.¹¹⁶

A fume exhaust system for cooking fumes has an odor filter that induces process catalyzing odors degradation under UV radiation.¹¹⁷ UV source is disposed upstream of the filter with respect to the fume exhaust stream flow direction.¹¹⁷ Titanium dioxide is used as a catalyst.¹¹⁷

An odor absorbing device uses a filter containing activated carbon.¹¹⁸ The filter is a granular coconut shell activated carbon, contained within a porous pouch.¹¹⁸

A vacuum filter bag with an odor-removing effect comprises a layer containing immobilized odor-retaining particles.¹¹⁹ Preferred odor-retaining particles are either carbon or zeolite or molecular sieves.¹¹⁹ Their contents are 4 to 8 wt% of the total weight of

the filter paper.¹¹⁹ Particles are fixed by the use of fixing agents, such as aluminum sulfate, polyaluminum chloride, polyaluminum nitrate, polyacryl amide, or polyethylene amide.¹¹⁹

Odor-containing air flow is directed to a filter which contains activated carbon or similar substance serving as a filtering material.¹²⁰ Particles contained in air flow are partially ionized and/or dissociated before entering odor filter.¹²⁰ Ionization and the subsequent reaction may convert odorous substances into reaction products which are odor neutral.¹²⁰ This diminishes the amount of odorous substances which have to be absorbed by the filter. Ionization is achieved by generation of plasma or electric discharges in air-flow.¹²⁰

An air filter works in the suction area over a cooking device.¹²¹ It has the form of a cartridge, plate, or pad.¹²¹ The filter material is activated carbon, zeolite or another odor-eliminating material.¹²¹

Biofilters and packed bed wet scrubbers are the most applicable odor control technologies for use in organics processing facilities (composting facilities).¹²² A life cycle assessment showed that the synthetic media biofilter had the highest environmental impact, followed by the wood chip media biofilter system.¹²² The packed-bed system had the lowest environmental impact.¹²²

11.15 SCAVENGERS

Polymer-supported (polystyrene or silica) p-toluenesulfonic acid is a highly effective, robust, economical and eco-friendly isocyanide scavenger.¹²³ The reversibility of hydrolytic fixation enables simple and straightforward regeneration and reuse of the reagents.¹²³

Odor and volatile organic compound emissions of natural flour-filled polypropylene composites were investigated in relationship to the zeolite type and content.¹²⁴ The thermal stability and degradation temperature of composites were slightly increased with increasing natural and synthetic zeolite content.¹²⁴ With natural and synthetic zeolite contents of 3%, odors and VOC emissions of the polypropylene/rice husk flour and polypropylene/wood flour hybrid composites were significantly reduced because of the absorption of the odor and VOC materials in the pore structures of the natural and synthetic zeolites.¹²⁴

Low odor fiberglass products have low trimethylamide emissions because the free formaldehyde in the resin has been scavenged with melamine, which resists thermal decomposition, and because binder contains a relatively low urea content, which is a trimethylamide contributor.¹²⁵ The resole resin production process includes the addition of two formaldehyde scavengers (melamine and urea) to produce modified phenol-formaldehyde resole resin. It can be used as a binder including fiberglass base material.¹²⁵

Packaging materials and packages that transfer off-odor eliminating compounds to foods and other products are disclosed.¹²⁶ It is a film containing the off-odor eliminating compound. A sulfur scavenging material is used as the off-odor eliminating compound.¹²⁶ It is applied to snacks, confections, baked goods, fresh plant materials, cereals, and beverages.¹²⁶ Sulfur scavenging compounds include a spray-dried mixture of C16-C18 acids, predominately the C16 acid, linoleic acid.¹²⁶ This material may contain a variety of other related compounds including palmitoleic acid, linolelaidic acid, linoelaidic acid, isolinoelaidic acid, *trans*, *trans*, *trans*-9,12,15-octadecatrienoic acid, and the like.¹²⁶ When compounded with LDPE its concentration is from 0.5 to 5 wt%.¹²⁶

The method of reduction or elimination of odors has been proposed for polyolefin-based products which undergo γ -irradiation sterilization.¹²⁷ Protection is given by an oxygen scavenger and additional use of an odor mask.¹²⁷ The oxygen scavenger is inserted into the package before sterilization.¹²⁷ The preferred oxygen scavenger is known under the trademark of FreshPax.¹²⁷ Other scavengers include copper-based compounds and vitamin C-based compounds.¹²⁷

Binder composition based on phenol-formaldehyde resin for making fiberglass insulation and other similar products contains copper or vanadium odor eliminating agent, such as cupric chloride, that, when cured, exhibits a lower amount of odor caused by the presence of trimethylamine.¹²⁷ Scavengers previously discussed can also be used.¹²⁵

Garment refreshing hangers incorporate activated charcoal into the body of the hanger.¹²⁹ The activated charcoal absorbs the odors, thus removing them from the garment.¹²⁹

Scavenger for aldehydes is used at the time of manufacturing a wood panel using wood materials and formaldehyde-based binder.¹³⁰ Sulfurous acid gas and hydrogen sulfide gas trap formaldehyde by chemical reaction.¹³⁰ Other aldehyde trapping additives include sodium and potassium sulfites or hydrazines.¹³⁰

Active nanocomposite films incorporate oxygen scavengers for packaging a variety of oxygen-sensitive food products.¹³¹ Multilayer packaging contained green tea extract as an antioxidant and free radical scavenger.¹³² A sensory analysis demonstrated that the packaged food was not affected by green tea extract, but it was well protected against oxidation, significantly reducing the rancidity.¹³² The formulator's guide to oxygen inhibition additives can be found elsewhere.¹³³

The odor scavengers used in cosmetics are selected from the group consisting of magnesium aluminum silicate hydrate, zinc oxide, kaolin, $\text{Cu}_2\text{CO}_3(\text{OH})_2$ (or malachite), and copper L-pyrrolidone carboxylate salt.¹³⁴

A polymeric film (PVDC) comprises odor absorbent layer.¹³⁵ The odor absorbent layer contains odor scavengers such as magnesium oxide, magnesium salt, magnesium hydroxide, zeolite, or their combinations.¹³⁵ Oxygen barrier properties are further enhanced by the incorporation of an oxygen scavenger.¹³⁵ The film is used in ostomy pouches.¹³⁵

11.16 ODOR-MASKING

Fragrances and deodorants for plastics are used in a variety of applications. They play an important role in food marketing, beverage packaging, and many consumer products.¹³⁶ The most frequent applications include:¹³⁶

- laundry baskets, storage containers, and sink stoppers
- stores (scents attract attention of customers)
- point-of-sale displays, white-goods showroom displays, and personal care packaging
- toys and games
- sachets filled with scented plastic beads and room air fresheners
- food and beverage packaging
- food processing (e.g., fresh-cut basil)

- closures of shampoo, laundry detergents, and another cleaning, health and beauty products
- garbage bags or household chemical containers (e.g., citronella)
- renovated offices (e.g., cedar used to mask odor from plastic materials)
- PVC (e.g., masking presence of sulfur stabilizers)
- pharmaceuticals and nutraceuticals (e.g, fragrances in container wall or in a desiccant canister to mask unpleasant odors of medicines or vitamins)

Results of drinking water studies demonstrate that chlorine has a masking effect on the detection of other tastes and odors.¹³⁷ When the total residual chlorine disappears in the network, other tastes and odors could be perceived by consumers.¹³⁷ When chlorine is low, other tastes and odors appear more clearly.¹³⁷ Chlorine can mask earthy/musty odors.⁹⁶ Chlorine can also mask geosmin and 2-methylisoborneol.¹³⁷

Odor-free hot-mix asphalt contains liquid asphalt and citrus terpene (4-isopropyl-1-methylcyclohexene) D-limonene mixed with vegetable oil.¹³⁸ The mixture contains 10-15 parts of terpene and 85-90 parts of oil.¹³⁸ About 0.5-1% of this mixture is added to asphalt to obtain asphalt to have no objectionable odor.¹³⁸

Two specific types of ingredients are added to cold or hot melt asphalt or coal tar for the dual purposes of holding, reducing, or complexing the obnoxious and toxic odors from asphalt while at the same time allowing a pleasant masking fragrance to predominate.¹⁴² The holding agents consist of various organic compounds which can bond or complex with, and effectively hold onto, other molecules.¹⁴² Typical complexing agents include dialkylglycol alkyl ethers and dialkylphthalates.¹⁴² Typical fragrances include natural and synthetic oils or extracts such as lemon oil, orange oil, peppermint, spearmint, cinnamon, bubble gum, and most other common fragrances.¹⁴² The concentrated extracts of fragrances consist of natural and synthetic materials having glycols, glycol ethers, alcohols, esters, aldehydes, ketones, and other compounds which can simply mask the obnoxious odors.¹⁴²

Organic polysulfide composition has an odor-masking compound selected from a group consisting of wintergreen, cinnamons, vanillins, terpenes, sesquiterpenes, or their combinations.¹³⁹ Such combination has more pleasant odor than polysulfide.¹³⁹

Styling shampoo composition contains a surfactant, cationic deposition polymer, malodor-producing hair styling polymer, odor-masking base, and water.¹⁴⁰ The odor-masking base comprises 15 to 75 wt% ionone, having a boiling point of >250°C, musk having a boiling point of >250°C, and highly volatile perfume having a boiling point of <250°C.¹⁴⁰ The highly volatile perfume may include 2-pentyloxy allyl ester, benzaldehyde, *cis*-3-hexenyl acetate, 2,6-dimethyl-7-octen-2-ol, para-tertiary-amyl cyclohexanone, n-decyl aldehyde, or their mixtures.¹⁴⁰

A device for enriching air for air disinfection, perfuming, and odor-masking is composed of the storage vessel, evaporating means, dosing means, and chemical components.¹⁴¹ Odor masking components are selected from a group of terpenes, corn starch, manganese salts, poly(vinyl pyrrolidone), and essential oils.¹⁴¹

An odor-masking substance is used by hunters, fisherman, and law enforcement officers to mask noisome odors.¹⁴³ Scents contained in the odor-masking substances can be selected from a group of wintergreen, spearmint, evergreen, and fruit.¹⁴³

Essential oil or essential oil components are included in the elimination of odors from oil-based media.¹⁴⁴ Preferred odor-reducing components are terpenes, especially d-limonene, l-limonene, dl-limonene, pinene, carene, terpinolene, camphene, myrcene, and sabinene.¹⁴⁴ Methyl ester of soybean oil is a preferred carrier oil.¹⁴⁴ Oil-based media typical of this application include candles, resins, fuel oil, waste oil fuel oil, synthetic lubricants, rubber, liquid asphalt cement, and hot mix asphalt.¹⁴⁴

An odor control fragrant additive comprises compacted pellets or granules infiltrated with fragrant oil.¹⁴⁵ Cellulosic material, activated carbon and binder are mixed together and compacted to produce pellets or granules.¹⁴⁵ The cellulosic material is preferably peat moss, which swells up during absorption of fragrant oil and acts as fragrant oil storage container.¹⁴⁵ Fragrant oil is delivered to activated carbon that has a large surface area, which evaporates the fragrance oil to release steady fragrance output.¹⁴⁵ Thus, the activated carbon, which evaporates fragrance provides a steady release of fragrance into the surrounding environment of fragrant compacted pellets or granules for a period of several months without overpowering the environment with excess fragrance.¹⁴⁵ The fragrant compacted pellets or granules may be used to suppress malodor from trash cans or litter boxes and may provide stand-alone additions to drawers and cabinets, emitting pleasant fragrance.¹⁴⁵ Representative examples of fragrance components include: volatile phenolic substances (such as iso-amyl salicylate, benzyl salicylate, and thyme oil red); essence oils (such as geranium oil, patchouli oil, and petitgrain oil); citrus oils; extracts and resins (such as benzoin siam resinoid and opoponax resinoid); synthetic oils such as Bergamot 37 and 430, Geranium 76 and Pomeransol 314, and Powder Mask CE-32907; aldehydes and ketones (such as β -methyl naphthyl ketone, p-tert-butyl- α -methyl hydrocinnamic aldehyde and p-tert-amyl cyclohexanone); polycyclic compounds (such as coumarin and β -naphthyl methyl ether); esters (such as diethyl phthalate, phenyl ethyl phenylacetate).¹⁴⁵

A solvent composition containing dimethyl sulfoxide has an odor-masking agent.¹⁴⁶ Odor masking agents are selected from several groups of fragrances, including monoester, diesters, triesters, alcohols, aldehydes, ketones, and terpenes.¹⁴⁶

Nanoencapsulation has a potential to protect sensitive bioactive food ingredients from unfavorable environmental conditions, alleviate incompatibilities, enhance solubilization, improve taste and odor masking, and lastly enhance bioavailability of poorly absorbable function ingredients.¹⁴⁷ The nanoencapsulation technologies include nanoemulsions, liposomes, solid-lipid nanoparticles, nanostructure lipid carriers, coacervation, nanoprecipitation, freeze drying, and spray drying, and these are discussed elsewhere.¹⁴⁷ Applications of encapsulation in beverage¹⁴⁸ and cosmetics¹⁴⁹ is also discussed.

11.17 ODOR-STRIPPING

Odors emitted by polyolefin materials are often a concern in the case of automotive interiors.¹⁵⁰ These emissions contain small amounts of volatile components that are formed during the processing of thermoplastics.¹⁵⁰ BYK has developed a new type of stripping agent: BYK®-P 4200 which significantly reduces odor.¹⁵⁰ The additive is a granulate, which is added to an extruder, with no further processing step required.¹⁵⁰ The effectiveness of BYK-P 4200 surpasses conventional solutions (e.g., adsorbents).¹⁵⁰

Steam stripping is used to remove odor-forming impurities from hop flavors.¹⁵¹ These impurities impart fruity, ester, fatty, or sour type of aromas.¹⁵¹ These impurities are

typically present in a concentration of 0.1 to 100 ppm.¹⁵¹ The pH should be adjusted to make steam stripping effective in removing impurities to produce the purified hop flavor.¹⁵¹ The pH should be adjusted to be between 8 and 11.¹⁵¹ Below pH 8, oil precipitation and decomposition can occur.¹⁵¹ Above pH 11, undesired base-catalyzed side chain cleavage of tetrahydroisovalpha acids can occur.¹⁵¹

A process of reducing volatile, odor-causing impurities in alkoxyated alcohols includes adjusting pH to be between 7 and 8.5 to produce an alkaline alkoxyated alcohol mixture for a period of time sufficient to produce a steam stripped alkoxyated alcohol containing a reduced amount of odor-causing impurities.¹⁵² If pH is above 8.5, color compounds are formed.¹⁵² The best odor reduction was obtained at pH of 7.2.¹⁵²

A stripping process is provided which continuously strips volatile substances from a dispersion containing polymer particles.¹⁵³ The volatile substances are stripped from a dispersion by blowing an inert gas into the dispersion to draw the volatile substances into the inert gas, removing the volatile substances from the gas mixture of the inert gas, and circulating the purified inert gas.¹⁵³ The stripping process is conducted at a temperature lower than 100°C to prevent agglomeration of the polymer particles.¹⁵³

A low odor aqueous styrenic polymer dispersion comprises acetoacetoxy or acetoacetamide functional polymer particles or acetoacetoxy or acetoacetamide additives and at least one organic amine having a high boiling point.¹⁵⁴ The aqueous polymer dispersion is useful for preparing coatings without the unpleasant odor of styrene containing dispersion.¹⁵⁴ Styrenic polymer dispersion is subjected to deodorization processes including both or either of steam stripping and carboxylesterase enzyme treatment.¹⁵⁴ The steam stripping can be proceeded for one to several cycles or passes to eliminate slight odor left in the dispersion.¹⁵⁴ The carboxylesterase can be added to the aqueous dispersion at room temperature, then stay overnight or follow the enzyme supplier's instruction to remove odorant substrates such as butyl acetate and butyl propionate from the dispersion.¹⁵⁴ The low odor coating composition is suitable for various styrene-containing coating systems, including acrylic, vinyl acrylic, styrene acrylic, powder, solvent acrylic, alkyd resin, solvent urethane, and epoxy coatings.¹⁵⁴ The low odor coating composition is suitable for application onto various substrates including bare or pre-painted substrates such as cement, ceramic, tile, painting, glass, plastic, wood, metal, woven and non-woven textile, and paper; extremely suitable for consumer products with olfaction requirements.¹⁵⁴

This invention relates to low odor stable coating compositions, including low odor stable paints, and methods of their production.¹⁵⁵ More specifically, it relates to stable aqueous coating compositions and paints comprising one or more emulsion-polymerized addition polymer and one or more carboxylesterase enzyme having an ester hydrolysis activity in the composition of less than 0.03 micromole/minute.¹⁵⁵ The inventive low odor coating compositions and low odor paints are obtained by reducing the carboxylester content (odor-causing component) by contacting the aqueous emulsion polymer with a carboxylesterase, either before, during, or after formulating the coating composition or paint.¹⁵⁵ Carboxylesterases that may be suitable to treat the polymer or coating composition include any enzyme referred to as an esterase, carboxylesterase or lipase.¹⁵⁵ The origin of the carboxylesterase may be animal, vegetable or microbial.¹⁵⁵ The enzyme may be used in solution or immobilized; preferably, the enzyme is soluble in the aqueous coating composition.¹⁵⁵ Preferred esterases are microbial in origin and include the fungal enzyme

cutin hydrolase (cutinase).¹⁵⁵ The amount of carboxylesterase which is used is preferably up to 3 ppm by solid weight of enzyme based on the weight of the aqueous coating composition.¹⁵⁵ Preferred is a pH greater than 8.¹⁵⁵ The contacting step may take place at a temperature of from about 25°C to about 65°C.¹⁵⁵ Steam stripping is more effective in combination with enzyme treatment.¹⁵⁵ For conventional steam stripping, VOCs that are more hydrophobic and normally retained in the polymer phase are more difficult to strip than VOCs that are more hydrophilic and contained in the aqueous phase.¹⁵⁵ Carboxylesterase converts hydrophobic VOCs into constituent hydrophilic alcohols and acids.¹⁵⁵ The carboxylesterase, in converting the hydrophobic VOCs to hydrophilic VOCs, converts more odorous VOCs to less odorous compounds.¹⁵⁵ As a result, it is easier to strip the composition to a lower odor with the same amount of steam because the material starts with a lower odor.¹⁵⁵

A method for removing volatile organic compounds from a latex using a membrane has been developed.¹⁵⁶ A VOC-containing latex flows on a surface of a membrane and a gas flows over the other side of the latex film.¹⁵⁶

The taste of water-soluble surfactants is improved by liquid-liquid solvent extraction.¹⁵⁷ The extraction solvent is selected from solvents having individual Hansen solubility parameters of a dispersion force component ranging from about 15 to about 17 (MPa)^{0.5}, a polar component ranging from 0 to about 9 (MPa)^{0.5} and a hydrogen bonding component ranging from 0 to about 11 (MPa)^{0.5} (e.g., food grade ethyl acetate).¹⁵⁷ The extraction solvent is able to extract (strip) odorous components of surfactant.¹⁵⁷

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REGULATIONS

European Union regulation gives a full list of flavoring substances permitted in food contact.¹ In addition to chemical name, table 1 of the regulation contains CAS number, information about substance purity, and restrictions on its use.¹ The table lists more than 3000 chemical compounds divided into 17 chemical groups.¹

FDA mentions odors under many parts of its regulation, including²

- 109: Unavoidable contaminants in food for human consumption and food packaging material
- 110: Current good manufacturing practice in manufacturing, packing, or holding human food
- 111: Current good manufacturing practice in manufacturing, packaging, labeling, or holding operations for dietary supplements
- 129: Processing or bottling of bottled drinking water
- 165: Beverages
- 172: Food additives permitted for direct addition to food for human consumption
- 173: Secondary direct food additives permitted in food for human consumption
- 174: Indirect food additives: general
- 178: Indirect food additives: adjuvants, production aids, and sanitizers
- 184: Direct food substances affirmed as generally recognized as safe
- 186: Indirect food substances affirmed as generally recognized as safe
- 201: Labeling
- 343: Internal analgesic, antipyretic, and antirheumatic drug products for over-the-counter human use
- 357: Miscellaneous internal drug products for over-the-counter human use
- 500: General
- 509: Unavoidable contaminants in animal food and food-packaging material
- 524: Ophthalmic and topical dosage for new animal drugs
- 700: General
- 740: Cosmetic product warning statements
- 801: Labelling

The above are the only few from numerous regulations regarding odor. Below we will comment on some sources which contain information about the past and existing regulations.

Migration and sensory changes of presterilized packaging materials have consequences regarding the quality of packaged goods and consumer safety.³ Therefore, migration and sensory properties of packaging materials have specific regulations.³ The effects of the formation of radiolysis products on overall migration, specific migration of food

additives or radiolysis products as well as on sensory changes are discussed in view of current European food law.³ According to EU regulations, the overall migration limit is 10 mg dm⁻².³ In the United States, radiolysis products as well as other polymer impurities are examined as “indirect food additives” which are subject to the “threshold-of-regulation” concept.³ This concept allows the migration of unidentified substances from the packaging material into the foodstuff as long as the daily concentration of 0.5 ppb per substance is not exceeded.³

The European and United States regulatory concepts regarding food-contact materials differ in fundamental approach.⁴ The European approach is based on the theory that all materials should be explicitly cleared and publicized in regulations based on a toxicological evaluation of the listed substances.⁴ In the United States, substances that are not expected to become components of food or are not likely to create public health problems do not require regulation because of minimal dietary exposure.⁴ The US approach applies the idea that “the dose makes the poison”, while the European approach requires toxicological data on all substances regardless of the level of anticipated exposure.⁴ The European Union’s Regulation 1935/2004 (last updated by Commission Regulation (EU) 2015/174) offered the opportunity for active packaging to be used in Europe by allowing the application of materials with agents that could migrate into foods.⁴

Odors are the major generators of public complaints to regulatory agencies in North America and Europe. Odor impacts are frequently regulated under the nuisance provisions of common law.⁵ For example, the Environmental Protection Act of Ontario, Canada states: “No person shall cause or permit to be caused the emission of any air contaminant to such extent or degree as may, (a) cause discomfort to persons; (b) cause loss of enjoyment of normal use of property; (c) interfere with normal conduct of business; or (d) cause damage to property.”⁵ Unfortunately, the conditions that establish whether a nuisance condition exists are not easily defined.⁵ There is a need to introduce objectivity into odor impact assessments and odor limits.⁵ Individual responses to odors are highly variable and can result in a variety of effects.⁵ The impacts of odors arise from a variety of interacting facts, such as frequency, intensity, duration, offensiveness, and location.⁵ In analysis of possible objective limits of odor exposure, the following statement was proposed: “Facilities that are identified as sources of potentially offensive odors shall ensure that the 10-minute average concentration of odor resulting from all sources at the facility and determined in accordance with accepted procedures, shall be less than 1 odor unit 99.5% of the time at the most impacted sensitive receptor.”⁵

In the USA, several odor regulatory approaches have been commonly used:⁶

- the use of ambient air limits for individual compounds such as hydrogen sulfide, methyl mercaptan, or total reduced sulfur⁶
- regulatory language that prohibits off-site nuisance or annoyance conditions as determined by field inspectors in response to complaints from the public (in some cases, inspectors rate odor according to a six point scale)⁶
- limits based on levels predicted by dispersion modeling and using the dynamic olfactometry approach with the criteria reported as odor units⁶
- best available control technology or similar approaches that specify required levels of odor treatment controls for new or upgraded large facilities⁶

- the American Society of Agricultural Engineering recommends setbacks from livestock facilities of 0.4 to 0.8 km for neighboring residences and 1.6 km to residential development⁶

In addition to these approaches, odor sampling and measurement standards exist which guide on how to obtain credible data.⁶ Also, olfactometer flow rates have been imposed that regulate the air flow rate from the olfactometer sniff points (1-10 cm/s).⁶

In Japan, the “Offensive Odor Control Law”, enacted in 1972, regulates offensive odors emitted from business activities in an aim to preserve the living environment and people’s health.⁷ The framework of the offensive odor control law includes designation of regulated areas, establishment of regulation standards, inspection, measurements, recommendation for improvement, order for improvement, and penalty.⁷ The following odor substances have been specified by regulation: acetaldehyde, ammonia, butyraldehyde, butyric acid, dimethyl disulfide, dimethyl sulfide, ethyl acetate, hydrogen sulfide, isobutyraldehyde, isobutyl alcohol, isovaleraldehyde, isovaleric acid, methyl isobutyl ketone, methyl mercaptan, propionic aldehyde, propionic acid, styrene, toluene, trimethylamine, valeraldehyde, valeric acid, and xylene.⁷ The Environment Agency of Japan drafted the amendment to the Law in 1995 in order to introduce the olfactory measurement using “triangular odor bag method”.⁸

In Lombardia, Italy, regional guidelines regarding odor emissions have been issued.⁹ Odor impact is assessed by dispersion modeling. Dispersion of plant odor emission within a radius of 3 km is evaluated.⁹ Odor annoyance is evaluated based on the measured intensity in odor units, distance from the odor source, and the type of communal area (e.g., industrial, residential, or commercial).⁹

Canadian federal legislation does not regulate odor emission. It is a responsibility of provinces and territories.¹⁰ Typically, 1-2 odor units are considered as potential impact in the residential area and 7 units in the industrial area.¹⁰ For some odorants, there are concentration standards in some provinces, for example, 15 $\mu\text{g}/\text{m}^3$ for H_2S (1 hr. average), or 100 $\mu\text{g}/\text{m}^3$ for ammonia.¹⁰

Similarly, in Australia, states have responsibility for setting air quality policies for odor.¹⁰ In South Korea, there are odor standards for 8 odorants.¹⁰

In Thailand, no factories shall discharge smelling air unless concentration does not exceed prescribed value.¹¹ Regulation specifies sampling and odor concentrations based on ASTM and JIS standards.¹¹

Comparison of odor regulations in several countries can be found elsewhere.¹² The regulations limits are expressed in odor units per sq. m (ou m^{-3}) as odor detection threshold.¹² Electronic nose is applied to measurement of odor concentration.¹²

The regional drinking water odorant regulation goals were based on the odor sensitivity distribution of the local population.¹³ The distribution of odor sensitivity to 2-methylisoborneol by the local population in Beijing, China was revealed by using a normal distribution function/model to describe the odor complaint response to 2-methylisoborneol episodes.¹³ The odorant regulation goals for the eight cities, developed by the local panels, varied greatly, from 12.9 to 31.6 ng/L, suggesting that a unified standard for 2-methylisoborneol may not be suitable.¹³

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HEALTH AND SAFETY

The relationship between odor detection by persons and health and safety effects of exposure are the subject of this chapter. Interventions for reducing air pollution are an important means of improving public health.¹ Most complaints by the public regarding pollution in their workplace or close to their homes are based on an olfactory determination by members of the public.

Two common effects of air pollution include annoyance and health-related symptoms.¹ The annoyance is a complex reaction which can be considered as a mixture of perception, emotions, and attitudes.¹ The health-related symptoms depend on the type of pollutant, such as gaseous pollutants and particulate matter.¹ Common gaseous urban pollutants include sulfur dioxide, nitrogen dioxide, and ozone, which cause pulmonary, but also neurasthenic symptoms, and eye, nose and throat irritations.¹ Particulate matter consists of dust and soot, which cause upper respiratory and pulmonary symptoms.¹ The relationship between the concentration of various pollutants and health problems are common knowledge but it is difficult to separate the influence of odor on health from simple annoyance.¹

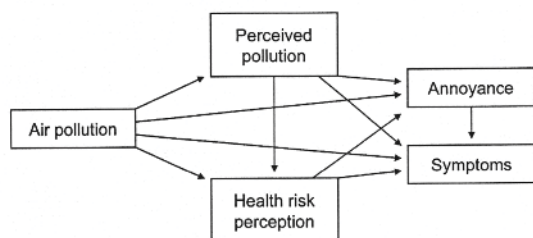


Figure 13.1. Analytic model of influences of air pollution, perceived pollution, health risk perception and annoyance on symptoms. [Adapted, by permission, from Stenlund T, Liden E, Andersson K, Garvill J, Nordin S, *Public Health*, **123**, 339-45, 2009.]

living in the neighborhood of a steel mill in Sweden, it was determined that health symptoms become a problem at far higher exposure levels than an annoyance. The perceived pollution was found to influence health risk perception and annoyance.¹ There was also a direct effect of air pollution on annoyance.¹ Health risk perception had an effect on annoyance and symptoms, whereas annoyance influenced symptoms.¹ This shows that relationships between all these parameters is extremely complex and can easily lead to errors in judgment.¹

Risk perception involves people's beliefs, attitudes, judgments and feelings.¹ Feelings may include worries of compromised health attributed to the environmental exposure.¹ But real effects are controlled by concentration, which is not well determined by sensory evaluation.¹ Figure 13.1 shows a model of influences of air pollution, perceived pollution, health risk perception and annoyance on symptoms of health problems.¹ In a study of a population

Study in Windsor, Ontario suggests that there are cumulative effects of outdoor air pollution and traffic noise on odor and noise annoyances and that annoyances have negative effects on both mental and physical factors of health related quality of life.⁸

Waste treatment processes produce odors and biological emissions to the surroundings, but their health effects are controversial.² The study of this problem was conducted in the surroundings of five large-scale Finnish waste treatment centers with composting plants.² The residents who were classified as “annoyed by odor” reported the following physical symptoms: unusual shortness of breath, eye irritation, hoarseness/dry throat, toothache, tiredness, fever/shivering, joint pain, and muscular pain.² The study showed that the physical symptoms were more likely associated with odor annoyance than with odor perception. In moderate odor conditions, health effects are mediated by annoyance.²

Life cycle assessment of the effect of the municipal solid waste site showed that trichlorofluoromethane and dichlorodifluoromethane accounted for more than 99% of impact potentials to global warming and approximately 70% to human toxicity (non-carcinogenic).⁷ The major contributor to both photochemical ozone formation and ecotoxicity was ethanol.⁷

Impairment of olfactory function in humans has been associated with occupational exposure to volatile chemicals.³ Workers with at least 4 years of exposure to styrene were examined in a study on the effects of exposure to loss of olfactory functions.³ There was no evidence that workers had any impairment of olfactory functions due to exposure.³ This is despite observations in animal studies that exposure to styrene at or below currently acceptable workplace limits produced lesions in the olfactory epithelium of rodents.³ These results strongly suggest that styrene at these exposure levels is not an olfactory toxicant in humans.³

Dampness and molds in a workplace building produce odors and are known reasons for sick building syndrome.⁴ In the studies conducted in Sweden, general, mucosal, and dermal symptoms improved when away from the workplace.⁴ Dampness in the floor construction in any workplace building was associated with the incidence of mucosal symptoms.⁴ Any dampness or molds at the baseline in the workplace building were associated with increased bronchial responsiveness and higher levels of eosinophilic cationic protein in serum and eosinophilic counts in blood at the baseline.⁴ The European Community Respiratory Health Survey conducting such studies is a multi-centre study performed in 48 centers in 23 countries throughout the Europe.⁴ This study is based on data from the center in Uppsala, Sweden.⁴ In a similar study, it was found that dampness at home decreased the remission of asthmatic symptoms.⁴ In office buildings, dampness increases chemical emissions from alkaline degradation of acrylate polymers in water-based glue or plasticizers in polyvinylchloride floor materials.⁴ This indicates that dampness in dwellings and workplace buildings can cause different types of health hazards.⁴ In Sweden, workplaces have better ventilation than homes, and less production of dampness.⁴ This means that the home has a higher relative air humidity, and surface condensation or wet surfaces (e.g., in the bathroom) which can cause mold growth more often in homes.

Frequently odors come from faulty products, as was the case of Chinese drywall used in US homes.⁵ In December 2008, the US Consumer Product Safety Commission received its first reports of odors, corrosion, and health concerns related to drywall originated from China.⁵ Homes, in which the drywall was installed, had higher hydrogen sul-

fide concentrations and greater rates of copper sulfide and silver sulfide corrosion compared to non-complaint homes.⁵ Carbonate and strontium in drywall was also elevated in complaint homes.⁵

Migration and sensory changes of sterilized packaging materials affect the quality of packaged goods and the consumer's safety.⁶ Migration and sensory properties of packaging materials are the subjects of specific regulations.⁶ Europe-wide accepted a standard for evaluation of impurities in packaging materials is still to be proposed.⁶ In the United States, radiolysis products, as well as other polymer impurities, are examined as "indirect food additives" which are suspected according to the "threshold-of-regulation" concept.⁶ This concept allows the migration of unidentified substances from the packaging material into the foodstuff as long as the daily concentration of 0.5 ppb per substance is not exceeded.⁶

Mosquitoes sense exhaled CO₂ and skin odor to find humans.⁹ Some odorants can be used as lures in mosquito traps.⁹ Inhibitors of the mosquito CO₂ receptor can mask attraction.⁹ Use of objective measurement method helps to find better solutions.⁹

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INDOOR AIR QUALITY

A large number of chemical substances are present in modern building products, household products, and furnishings.¹ They have the potential for chemical reactions in the material, on the material surface, and in the gas phase.¹ These indoor compounds are a source of primary and secondary emissions.¹ The primary emissions are related to the original raw materials included in building products, whereas the secondary emissions are products of chemical reactions, such as reactions with components of air (O_3 , NO_2 , OH, peroxyacetyl nitrate, and peroxypropionyl nitrate).¹ In other words, oxidation and reactions with free radicals cause compositional changes in materials, causing odors and volatile components.¹ Hydrolysis is the other common reaction which leads to the modification of original building materials and produces odors and VOCs.¹ Elevated temperature during production of building materials is also a cause of changes in chemical composition resulting in odor formation.¹ Also, reactions between different raw materials and products of the above decomposition products may cause odor formation in an indoor environment.¹ Finally, metabolic reactions caused by various microorganisms are also known contributors to indoor pollution.¹ There are many sources of indoor air pollution. They include: wood and wood-based products, linoleum, eco-lacquers, nitrocellulose lacquers, alkyd resins, cork, UV-cured coatings, solvents, stabilizers, plasticizers, flame retardants, acrylate coatings, styrene butadiene rubber, rubber, vulcanization accelerator, foaming agents, casein products, water-based paints, flexible polyurethane foams, sealants, adhesives, and many more products.¹

2-Ethyl-1-hexanol is sometimes detected in indoor air at relatively high concentrations.² Figure 9.2 shows a schematic diagram which explains the reason for its formation, which is caused by hydrolysis of PVC plasticizer contained in PVC flooring.² Hydrolysis occurs in the presence of moisture migrating from moist concrete slabs.² The type of adhesive influences the process of hydrolysis, since some components of adhesive may suppress hydrolysis.² 2-Ethyl-1-hexanol is considered to be one of the causes of odor in the indoor air and sick building syndrome.²

Association between dampness and indoor molds in workplace buildings and selected biomarkers were studied in relationship to incidence and remission of sick building syndrome.³ The 10-year incidence of general, mucosal, dermal symptoms, and any symptom that improved when away from the workplace was 7.2%, 11.6%, 6.4%, and 9.4%, respectively.³ The 10-year remission of general, mucosal, dermal symptoms and work-related symptoms was 71.4%, 57.1%, 70.4%, and 72.2%, respectively.³ Dampness and molds in the workplace building were associated with increased incidence and decreased remission of sick building syndrome and increased bronchial responsiveness and eosinophilic inflammation.³

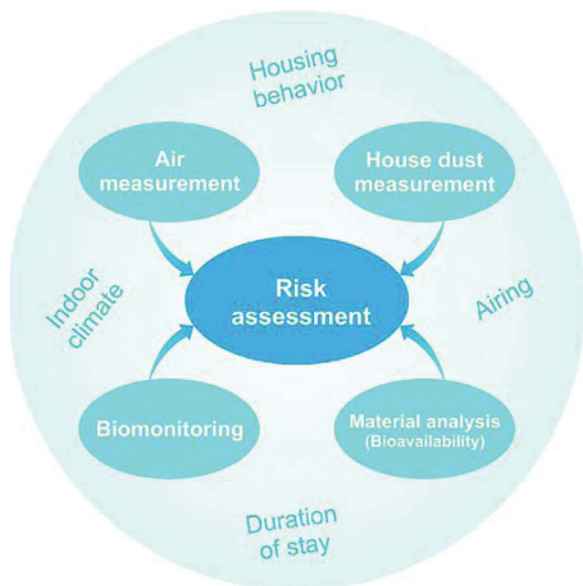


Figure 14.1. Parameters in risk assessment from chemical compounds in the indoor environment. [Adapted, by permission, from Wensing M, Uhde E, Salthammer T, *Sci. Total Environ.*, **339**, 19–40, 2005.]

In the indoor environment, phthalic acid esters (plasticizers) and phosphororganic compounds (flame retardants) are released from a number of sources under normal living conditions and accumulate in air and dust.⁴ Evaluation of indoor exposure to phthalates and flame retardants requires the determination of the target compounds in indoor air and house dust as well as emission studies.⁴ Figure 14.1 shows the relationship of parameters in risk assessment in an indoor environment.⁴ The results of studies show that the flame retardant concentration obtained, while the car was driven, were below the Federal Environmental Office's recommended guideline values.⁴ It can be anticipated that very low air concentration of phthalates will be detected

when the car is operated, especially because of high air exchange rate under normal conditions of car operation.⁴ In household studies, it was determined that di(2-ethylhexyl) phthalate was present in concentration of 74% of acceptable daily intake value for infants under worse case scenario conditions, and below 10% if long-life exposure is considered.⁴

The odor was reported by information technological office personnel in a medical center in Taiwan after the office was refurbished.⁵ Carbonyl chemicals and volatile organic compounds were investigated.⁵ The odor was also evaluated and correlated with chemical emissions.⁵ Nonanal and decanal were found to be possible chemicals causing odors.⁵ The concentration levels of these two chemicals in the complaint area are higher than those in the non-complaint areas and they exceeded odor thresholds.⁵ These long-chain aldehydes were formed during the oxidation degradation of fatty acids, such as linoleic, linolenic, and oleic acids, which are ingredients of linoleum and surface coatings used during refurbishing.⁵ To reduce odor, effective ventilation flow rate was provided to reduce the concentrations of odorous chemicals.⁵

Chemical pollutant concentrations have been found to contribute to sick building syndrome.⁶ Higher total VOC levels were detected in indoor air ($1.33 \pm 1.53 \text{ mg/m}^3$) than in outdoor air ($0.71 \pm 0.46 \text{ mg/m}^3$).⁶ Ethanol, acetone, isopropanol, 1-butanol, acetic acid, acetonitrile, and 1-methoxy-2-propanol were determined in indoor air.⁶ It was found that the source of these VOCs was manipulation of solvents in the basement of the building.⁶

Health complains and annoyances resulted after moving into a new office building.⁷ Overall concentrations of volatile organic compounds and formaldehyde were fairly low.⁷ High concentrations (4300–7800 mg/kg) of tris-(2-butoxyethyl)-phosphate and di(2-ethyl-

hexyl) phthalate (980—3000 mg/kg) were found in dust samples.⁷ The coating of the rubber floor was identified as the source of tris-(2-butoxyethyl)-phosphate, while no single predominant source of di(2-ethylhexyl) phthalate was found.⁷ After removal of the coating of the rubber floor, the concentration of tris-(2-butoxyethyl)-phosphate was reduced by 90%.⁷ Tris-(2-butoxyethyl)-phosphate together with unfavorable indoor conditions (low humidity and high temperature) were responsible for the development of the complaints.⁷

The above two examples show that in some cases odor complains are caused by the use of building materials which are not suitable for indoor environments.

The concentration of volatile organic compounds, including formaldehyde, in classrooms, kindergartens, and outdoor playgrounds of three primary schools were measured in spring, winter, and fall in Izmir, Turkey.⁸ Benzene, toluene, and formaldehyde were the most abundant compounds with indoor air concentrations of 29, 87, and 106 $\mu\text{g}/\text{m}^3$, respectively.⁸ In addition, naphthalene, xylenes, and isomers of dichlorobenzene were also found.⁸ Formaldehyde was the most dangerous pollutant with high chronic toxic and carcinogenic risk levels according to the health assessment followed by naphthalene, benzene, and toluene due to their chronic effects.⁸ Seasonal variations in VOC concentrations, including formaldehyde, have also been reported for primary school classrooms, kindergartens, and outdoor playgrounds.⁸

Dampness, pets, and environmental tobacco smoke early in life and asthma in Taiwanese children were correlated.⁹ Childhood asthma was associated with exposure to cockroaches, visible mold, mildew odors, carpet, pets, and more than one hour of environmental tobacco smoke per day.⁹

Perception of odor were strongly associated with the risk of children's asthma and allergies in study conducted in Baotou, China.¹⁴ Significant risk factors were family history of asthma or allergies, living near a main road or highway, evidence of moisture related problems, and never exposing bedding to sunshine.¹⁴

A sensor system, having 38 non-specific gas sensors, was used to analyze a wide range of different volatile compounds.¹⁰ Emissions from building products were analyzed in relationship to indoor pollution.¹⁰ The model used for analysis was able to map the odor intensity to the sensor signal pattern in order to predict the odor intensity caused by the investigated building products. Humidity had an influence on readings.¹⁰

Concentrations of formaldehyde, both personal and stationary, are on average in the order of 0.05 mg/m^3 or less in Europe and North America with the exception of new housing or buildings with extensive wooden surfaces, where formaldehyde concentration may exceed 0.1 mg/m^3 .¹¹ Its effect on the eyes and airways occurs around 0.6–1 mg/m^3 .¹¹ An air quality guideline of 0.1 mg/m^3 (0.08 ppm) is considered protective against both acute and chronic sensory irritation in the airways in the general population.¹¹

Odor has a strong relationship with symptoms of sick building syndrome.¹² Odor threshold ratio, which can be obtained by dividing the concentration level of each chemical by its odor threshold ratio value, was used to evaluate the health effect of 53 chemicals.¹² The total volatile organic chemicals concentrations in laboratories varied from 212 to 17,200 $\mu\text{g}/\text{m}^3$, and the major chemicals detected in indoor air were α -pinene, limonene, camphene, paracymene, and 2-butanone.¹² The chemicals which exceeded 10 odor threshold ratios were acetic acid, acetaldehyde, propanal, pentanal, hexanal, nonanal, decanal,

pinene, para-cymene and limonene.¹² Odor threshold ratio is a useful indicator to evaluate the health effect of indoor air chemicals in addition to total volatile organic compounds.¹²

Polymer filters treated by plasma-assisted graft polymerization, nonthermal plasma, and plasma-assisted graft polymerization followed by nonthermal plasma treatment were developed for use as multifunctional filters that can simultaneously remove odor and particulate.¹³ A nonthermal plasma-treated filter can adsorb a large amount of ammonia, but its performance deteriorates after one month of use, whereas plasma-assisted graft polymerization followed by nonthermal plasma treatment offers filter which deteriorates only slightly.¹³

The polluting impact of fireplaces powered by liquid or gel bioethanol based fuels, with a special focus on their odor emissions was conducted to provide the European Commission information useful to define the guidelines for a dedicated legislation.¹⁵ The average odor emission factors reached values between 40 and 110 [100 ouE kJ⁻¹] during the shutdown, but they were below 10 during the operation periods.¹⁵ The electronic nose can be a valid additional instrument in activities aimed at evaluating the indoor air quality.¹⁵ Its use as an odor detector and as an integrated device in air ventilation systems for indoor environments is proposed.¹⁵

Emissions from various scented consumer products have been investigated.¹⁶ More than 300 potentially odorous compounds were identified in all products.¹⁶ Limonene and linalool were the most frequent EU-regulated fragrance allergens.¹⁶ Eugenol was one of the most frequently detected compounds in the candle emissions.¹⁶

Accurate identification and quantification of the secondhand tobacco smoke that drifts between multiunit homes was conducted to assess residents' exposure and health risks.¹⁷ There is evidence of the secondhand tobacco smoke intrusion in all units studies-during the monitoring period.¹⁷

The general public is now aware of the relationship between indoor air quality and human health.¹⁸ Volatile odorants can be released at significantly high concentration levels from some non-decayed foods.¹⁸ The emission concentrations of NH₃ and trimethylamine increased significantly with the aging of food samples under low-temperature conditions of the refrigerator.¹⁸ H₂S, CH₃SH, and trimethylamine were identified as the major odorant components.¹⁸

Increased household energy efficiency may increase risk of current asthma.¹⁹ A moldy/musty odor was associated with a two-fold increased the risk of asthma because of reduced ventilation.¹⁹

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