Mineral oil transfers to food

Strategies for preventing the migration of MOSH/MOAH



Our Author: Prof. Dr. Reinhard Matissek, Director of the Food Chemistry Institute (Lebensmittelchemisches Institut – LCI) of the Association of the German Confectionery Industry (Bundesverband der Deutschen Süßwarenindustrie – BDSI), Cologne, Germany

ineral oils are widely found in the environment. Their components can migrate not only into plant-, but also into animal-based food via various different ways. They are comprised mainly of mineral oil saturated hydrocarbons (MOSH) and to a lesser degree of mineral oil aromatic hydrocarbons (MOAH). Both are easily absorbed into the body from food and can accumulate in the body's fat cells and in some organs. Animal tests form the basis of toxicological assessments, because currently there are no studies on the effects of MOSH and MOAH on humans. According to the Federal Institute for Risk Assessment (Bundesinstitut für Risikobewertung – BfR), the intake of MOAH should be avoided altogether since it cannot be ruled out that this fraction contains carcinogenic compounds.

The main route of entry of mineral oil components into foods is not caused by the food manufacturers themselves. Among other things, it has been determined that MOSH/MOAH migrates from packaging made from recycled waste paper, and it would be helpful if, for example, newspaper publishers also used mineral oil-free printing ink in order to prevent this. But in addition to packaging material, there are many other routes of entry which have already been identified as well as putative ones which have not yet been studied. Current research programmes are attempting to identify them. In view of the fact that mineral oil components are widely found in the environment, that there are many different



Online coupling of Liquid Chromatography with Gas Chromatography and Flame Ionization Detector for the quantification of the sum of MOSH and MOAH (Instrument from Axel Semrau Company, Sprockhoevel/Germany)

ways in which MOSH and MOAH can get into foods, the sophisticated analytic methods and the number of players involved, the topic is very complex and the challenges are numerous and great.

The transfer of mineral oil components into foods is a topic that the food industry is taking very seriously. A joint effort by all the members of the value chain – from the farming sector to the raw materials trade, the transportation sector, the food, packaging and printing ink industry, including newspaper publishers, all the way through to the food trade and consumers – is being initiated by the German Federation for Food Law and Food Science (Bund für Lebensmittelrecht und Lebensmittelkunde – BLL) in order to minimise and prevent the migration of mineral oil components into food. Together with the packaging and printing ink industry, as well as with all the other members of the value chain, food manufacturers are looking for ways to avoid and minimise the migration of mineral oil components into food - but it takes time. In the summer of 2013, the Association of the German Confectionery Industry (Bundesverband der Deutschen Süßwarenindustrie – BDSI) launched a cross-sectional minimisation initiative for its own sector and invested about half a million Euros in stateof-the-art laboratory equipment for its own Food Chemistry Institute (Lebensmittelchemisches Institut – LCI). The main objective is to minimise and prevent the transfer of mineral oil components to confectionery and savoury snacks and to develop safe and reliable analytic methods.

Introduction

That mineral oil components can migrate into food was first discovered by research done at the Zürich Canton Laboratory/ Switzerland. At that time, the cause was identified as cardboard made from recycled paper which can contain mineral oil [1]. As a rule, mineral oil enters the recycling process via the mineral oil-based printing ink generally used to print newspapers. Unwanted mineral oil components can thus migrate from the packaging into the food through the gas phase. Initially, the evidence pertained only to dry food packaged directly in cardboard or paper and with a large surface area, e.g. rice, flour and noodles; later, fatty food such as pizza was also seen to be affected. But mineral oil components were also found in foods of plant and animal oriain that was not packaged in cardboard or paper, for example in eggs, sausage and fish, as well as in vegetable oils, chocolate, bread and bread rolls. In the meantime, several more sources of contamination have been identified. Therefore, not only is more research needed in order to avoid and minimise contamination, but all the members of the manufacturing chain need to work together: from the farming sector to the raw materials trade, the transportation sector, the food, packaging and printing ink industry including newspaper publishers all the way through to the food trade and consumers. Some of them – including the Food Chemistry Institute (Lebensmittelchemisches Institut - LCI) of the BDSI in Cologne - have already been cooperating with the scientific community and public authorities for some time.

MOSH and MOAH: What are they?

Mineral oils are basically made up of two chemically and structurally disparate



tri-aromatics

Figure 1: Examples of the different classes of hydrocarbons found in crude oil: R indicates branched or unbranched alkylgroups with 0>20 C-atoms [2]

fractions. The main fraction, with a share of between 75 and 85 percent, consists of so-called MOSH (mineral oil saturated hydrocarbons); the smaller fraction, with a relative share of between 15 and 25 percent, is made up of so-called MOAH (mineral oil aromatic hydrocarbons). Both fractions consist of carbon chains that usually have fewer than 25 carbon atoms (< C25). MOSH are saturated, paraffin- like i. e. open-chained, usually branched and naphtenic (cyclic) hydrocarbons with low to medium viscosity. MOAH are made up of a large number of different aromatic hydrocarbons which consist mainly of one to four ring sys-

tems, and of which up to 97 percent are alkylated (see Figure 1).

How do mineral oil components can find their way into foods?

Mineral oils are widely found in the environment. Their components can migrate into foods via various different ways. Hence an environmentally caused "basic contamination" of raw materials occurs, e.g. through combustion processes (i. e. petrol engine, emissions, industrial plant emissions, forest fires, etc.) and particulate matter from tarmac roads. Contamination can also begin before and during harvesting due to pesticides or through lubricants and hydraulic oils from harvesting machines, or afterwards due to the treatment of crops with agents that contain mineral oil, e. g. antifoam/anti-caking agents, or through treating rice with dust binders (anti-dusting) or for more gloss (spraying). Figure 2 depicts various potential sources of contamination, using rice as an example.

In addition, mineral oil components can migrate into raw materials during transport from transport packaging contaminated with mineral oil. Impregnated jute and sisal sacks are one example [3] (see also the explanations in the box).

Furthermore, contamination with mineral oil can occur during the food manufacturing process, e. g. due to oiling machine parts or through grease that is used during maintenance and cleaning [2].

Another route of entry which we are already familiar with is through cardboard packaging: Recycled cardboard boxes can contain mineral oil-based printing inks from the recycled paper. This is the reason why food packaging is now usually manufactured from virgin paper. However, that is neither the case for secondary packaging used during transport, nor for packaging stored next to food during transport, in retail stores or in households, from which mineral oil components can also migrate into foods. There are proven cases of food which has left the manufacturing plant uncontaminated by MOSH/MOAH, and into which mineral oil components have subsequently migrated during the transport or storage process.

In addition to the mineral oil present in recycled cardboard, the mineral oil-containing printing ink used to print the packaging can be a source of migration for mineral oil components. At least in food packaging,



Figure 2: The various cources of MOH potentially contaminating rice: proporion of samples being affected (in percent) against the concentration expected (mg/kg). Estimates in the figure are intended for illustration of the principles [2]

this source has been almost entirely eliminated, since the food industry has mostly converted to printing its packaging with ink that contains little or no mineral oil. Mineral oil-containing glue, which is used for manufacturing packaging materials, may also be a route by which mineral oil components can migrate into foods.

In the case of dry food stored at room temperature, migration into the food is effected via evaporation, transport in the gas phase and re-condensation in the food. As a result, this kind of migration is restricted to mineral oil components that have a certain vapour pressure (e. g. hydrocarbons < C25). Inner packaging made from paper, polyethylene (PE) or polypropylene (PP) slows migration, but does not completely prevent it. Only packaging containing aluminium and polyethylene

Jute and sisal sacks are often used to transport raw materials. In order to make it easier to manufacture sacks from the fibres, the latter are treated with socalled ,batching oils' which might conceivably also contain mineral oils. As far back as 1998, the International Jute Organisation (IJO) published a recommendation on the purity requirements for batching oils. According to their specifictions, jute sacks that come into direct contact with food may only contain non-toxicsubstances and should also not transmit any off-flavours or off-tastes onto foods. For jute sacks destined to come into contact with cacao beans, coffee beans and shelled nuts, the IJO determined – in addition to its general specifications – a maximum value for unsaponifiables of less than 1,250 mg/ kg jute fibre. At that time, the decision was made to determine the unspecific sum parameter unsaponifiables so that regulations could be monitored with the help of basic laboratory equipment in the countries manufacturing the sacks – without having to depend on mineral oil hydrocarbon analysis with large analytical apparatuses, a procedure which tends to be very complex. In its 2004 statement on the use of mineral oils in jute and sisal sacks, the European Food Safety Authority (EFSA) endorsed the IJO-recommendations listed above from a toxicological perspective [4]. terephthalate (PET) is considered to be migration-proof, as so-called 'functional barriers' [5, 6]. However, these also have disadvantages: Manufacturing aluminium foil for inner packaging or to coat cardboard is not only a very energy-intensive process, but also has drawbacks during the recycling process and is harmful for the environment. Using foil that is impermeable for water vapour can also lead to an increase in the growth rate of microorganisms in the food [5]. Innovative special foils have recently been developed, but presumably these will only be suitable for certain packaging systems.

Toxicology of MOSH and MOAH

Almost 90 percent of shorter-chained hydrocarbons such as MOSH and MOAH are readily absorbed into the body. MOSH can accumulate in the body's fat cells and in organs such as the lymph nodes, spleen and liver [2]. The concentrations of mineral hydrocarbons in fatty tissues (about 60 mg/kg on average) are similar to those in breast milk [7]. Animal studies have shown that mineral oil mixtures with low viscosity can lead to inflammation in the liver, the heart valves and to histiocytosis in lymph nodes [8]. To date there are no toxicological studies on the effects of mineral oil absorption on humans.

As a consequence, toxicological assessments are based on the results of animal studies and up till now were made by the Joint FAO/WHO Expert Committee on Food



Figure 3: Depiction of a so-called chromatographic "hump" [according to 9]

Additives (JECFA), the EFSA and the BfR. In 1998, the temporary acceptable daily intake (ADI) for MOSH (so-called category II/III mineral oils < C25) was specified as 0.01 mg/ kg body weight per day, but was retracted in 2012 because there was no expertise. According to the BfR, the intake of mineral oil mixtures with high aromatic content (MOAH) should be avoided altogether, since it cannot be ruled out that the MOAHfraction contains cancer-inducing aromatic compounds (or possibly also polycyclic aromatic hydrocarbons – PAHs).

A recent assessment by the EFSA in May of 2012 is based on the assumption that the intake of adults is 0.03 to 0.3 mg/kg body weight per day. At a No-Observed-Adverse-Effect-Level (NOAEL) for MOSH of 19 mg/kg body weight this leads to a margin of exposure (MOE) of 59 to 690. There are plans to adjust the former ADI for MOSH because of these new toxicological assessments by the EFSA [2].

To date, there is no standardised method for analysing MOSH and MOAH

Analysis procedures for determining levels of mineral oil traces in foods are highly complex and demanding, since it involves a complex mixture that needs to be quantified as the sum of all its components. It is impossible to analyse the individual components due to the huge number of compounds. That is why the gas chromatological analysis of complex mineral oil mixtures does not yield sharp peaks, but very broad signals instead. Analysts call these a chromatographic "hump" or "unresolved complex mixture" (UCM) (see Figure 3).

The easiest way of analysing MOSH and MOAH is with current state-of-the-art technology, namely with the help of online



GD2=specification of a recycled cardboard

Mineral oil content

Figure 4: Reduction of mineral oil content in recycled cardboard packaging from 1980 to 2010 [12]



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... more information info@axel-semrau.de coupled liquid chromatography-gas chromatography-flame ionisation detection (LC-GCFID). No standardised reference method for analyzing mineral oil components, which has also been tested in ring trials, is available to date. Analysis is also often made more difficult by other oligomeric structures, socalled polyolefin oligomeric saturated hydrocarbons (POSH), which can migrate into foods from polyethylene (PE) or polypropylene (PP) films and which cannot be analytically distinguished from MOSH and MOAH.

Chances of minimising and avoiding MOSH and MOAH in foods

From the perspective of the BfR, the Federal Ministry of Food, Agriculture and Consumer Protection (Bundesministerium für Ernährung, Landwirtschaft und Verbraucherschutz - BMELV), the Federal Environment Agency (Umweltbundesamt – UBA) and also the food industry, a key source of the migration of mineral oil components into foods could largely be eliminated if mineral oil-free ink was used in news-paper printing. According to the UBA, a total of about 70,000 tonnes of mineral oil enter the European paper cycle and could very effectively be avoided if all offset printing processes were switched to mineral oil-free ink - at a comparatively low total cost [10]. Although it would be most effective to address the problem where it originates, only very few newspaper publishers are currently willing to do so. The newspaper industry says that this step would accrue enormous costs, among other things, but also points out the substantial amounts of imported waste paper and products which, in its opinion, would counteract the effectiveness of measures taken on a national level [11].

The food industry takes the topic of contamination with mineral oil very seriously and has been trying for years to minimise the migration of mineral oil components into foods in those areas in which it can exert its influence directly. The packaging industry is also active: For example, since 1980 it has managed to continuously lower the amount of mineral oil in recycled cardboard packaging to less than 20 percent of its initial value (see Figure 4).

The following approaches to reducing the content of mineral oil in food have already been implemented, are components viable or are being tested:

• Using packaging manufactured from virgin fibres instead of using recycled

Food chain Potential sources - overview



Potential sources for MOSH/MOAH entries - Overview

cardboard for packaging (is being implemented by many food manufacturers. However, since mineral oil components can migrate into foods from transport packaging or adjacently stored packaging, this is only a partial solution. The UBA does not advocate this approach, since using recycled paper is more sustainable and environmentally friendly.).

- Converting to migration-poor and/or migration-free ink when printing packaging (as a rule, the food industry implements this approach).
- Using functional barriers between food and packaging cardboard, e.g. coating the inside of packaging with aluminiumor PET-films (laminates) or using inner bags or specialised films coated accordingly (is already being implemented by some companies and is being tested by others. Drawbacks: Composite packaging is more difficult to recycle and manufacturing aluminium is energy-intensive, so the total environmental balance is negative. Using foil that is impermeable for water vapour can also lead to an increase in the growth rate of microorganisms in the food so it - like special types of film - isn't suitable for every kind of food.).
- Minimising the use of waste paper with high concentrations of mineral oil when manufacturing packaging made from recycled paper (is already being implemented by the paper industry).
- Rinsing the ink out of newspapers (deinking) during the recycling process and

cleaning recycled waste paper designated for packaging food much more effectively, as is already being done when manufacturing hygiene paper (not a very promising method, since only small amounts of mineral oil are removed).

Strict implementation of the IJO-recommendations on treating jute and sisal sacks, i. e. treating them only with batching oils that are free of mineral oils (is being required by confectionery manufacturers and suppliers of raw materials; consistent compliance in the countries of origin and during further transport is important in order to avoid contamination even before food is manufactured).

Furthermore, it would be essential to implement measures to at least reduce the migration of mineral oil components via the many other routes of entry described above, e.g. via the environment and machines, since the problem of contamination cannot be solved by modifying packaging alone. In order to do so, it is vital to further advance research into the sources of contamination, but also to define a standardized reference method for analysis and to intensify the analysis of samples across the entire chain of farming, food manufacturing and processing.

German confectionery industry is intensifying its research

The potential migration of mineral oil components into foods is not an issue specific to confectionery; it affects the entire food industry. For its own sector, the Association of the German Confectionery Industry (Bundesverband der Deutschen Süßwarenindustrie - BDSI) has intensified its activities geared towards consumer health protection. Because the BDSI has its own state-of-the-art institute, the Food Chemistry Institute (Lebensmittelchemisches Institut – LCI), it is ideally set up to do so. Since the topic has come to the fore, the Institute has identified sources of contamination, evaluated methods of analysis and highlighted ways of solving the problem. By intensifying their collaboration with a research laboratory such as the LCI, manufacturers can receive valuable advice and recommendations and, if necessary, can implement measures accordingly.

In the summer of 2013, the BDSI is also initiating a research project due to run three years, which will focus on the topics of analysis, contamination sources and minimisation strategies for industry (see also the box below). During the course of this project, the BDSI and the LCI will also continue to liaise closely with every member of the value chain and to cooperate with them, since this is the only way of minimising the migration of mineral oil components.

Since the topic is and can be relevant for every kind of food, the BDSI is also exchan-

ging information with other sectors of the food industry. It has been corresponding closely with packaging suppliers of the confectionery industry for some time in order to prevent and reduce as much as possible the migration of mineral oil components and other unwanted substances by the targeted choice and design of packaging material and packaging concepts. The LCI is also actively participating in the relevant working group of the BLL.

Measures planned by the German federal government

The BMELV is in the process of preparing two national regulations regarding mineral oil residue in food. The so-called "regulation on printing ink" (Druckfarben-Verordnung) is supposed to legislate, among other things, that printing ink may only contain certain toxicologically assessed substances listed in a positive list. Among other things, this means that in future, ink that contains mineral oil may not be used to print food packaging. The scope of the legislation does not extend to newspaper publishers. A second regulation - the socalled "regulation on mineral oil" (Mineralöl-Verordnung) - aims to prevent MOAH from packaging made from recycled paper from migrating into foods [13].

Continuation, LCI-research in the context of the BDSI's minimisation initiative

Within this context, the LCI will also participate in ring trials and will cooperate with other laboratories. It will also coordinate its research activities with the Federal Institute for Risk Assessment (Bundesinstitut für Risikobewertung – BfR) and the Federal Office of Consumer Protection and Food Safety (Bundesamt für Verbraucherschutz und Lebensmittelsicherheit – BVL).

LCI-research in the context of the BDSI's minimisation initiative

The objective of research at LCI is to prevent the migration of MOAH into confectionery and savoury snacks and to minimise the migration of MOSH as much as possible. Armed with stateof-the-art equipment for online coupled liquid chromatography-gas chromatography-flame ionisation detection (LC-GCFID) and multi-dimensional gas chromatography-mass spectrometry (GC x GC-TOF), the LCI will intensify its current research and focus on the following aspects in particular:

- Developing and establishing analytic methods
- Analysing samples of raw materials, packaging materials and food in all their processing and storage phases in order to identify from exactly where MOSH and MOAH are migrating into them
- Setting up a database which will allow not only the tracking of migration of mineral oil components, but also the sources of contamination
- Recognising the various factors which impact the
- migration of mineral oil components into foods

The mineral oil legislation initiated by the BMELV does not do justice to the diverse challenges that arise solely from the complexities of the way MOSH and MOAH migrate into foods. The fact that the migration of mineral oil components cannot be solved by the food industry alone and not just on a national level is being ignored. Not much can be achieved if Germany forges ahead alone. Although specialists have begun discussing the issue on a European level, no legislative initiative is currently in sight.

Conclusion

The transfer of mineral oil components into food is a topic that the food industry is taking very seriously. A joint effort by all the members of the value chain - from the farming sector to the raw materials trade, the transportation sector, the food, packaging and printing ink industry, including newspaper publishers, all the way through to the food trade and consumers - is necessary in order to minimise and prevent the transfer of mineral oil components into foods. In view of the fact that mineral oil components are widely found in the environment, that there are many different ways in which MOSH and MOAH can get into foods, the sophisticated analytic methods and the number of players involved, the topic is very complex and the challenges are numerous and great.

Some measures to improve packaging have been implemented to date. Preventative strategies need to be rigorously implemented before the food manufacturing process begins. Because: The issue cannot be solved just by modifying packaging.

However, currently not all sources of entry have been identified nor have known routes of entry been researched so that further solutions can be found. There is also no standardised reference method that has been tested in ring trials available for analyzing mineral oil components. This highlights the fact that further research is necessary and that successfully minimising or reducing MOSH and MOAH will take time.

Together with its own research laboratory LCI and its member companies, the BDSI is implementing its own comprehensive plan to minimise and prevent the transfer of MOSH/MOAH, which is focusing on analytic methods and sources of entry in particular – thus broadening the knowledge base – and on promising and practical prevention strategies for industry. To this end, the BDSI has invested about half a million Euros in new laboratory equipment in the summer of 2013. The results of these activities will inform the discussion with all the members of the value chain, above and beyond the confectionery industry.

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