

STATE-OF-THE-ART REPORT



Concrete Release Agents and the Environment

4th Edition, June 2015



Imprint

4th Edition, June 2015
Deadline: May 2015

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213-SB-E-2015

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Design

stationreal marketing und kommunikation gbr, Frankfurt am Main
www.stationreal.de

Source of photographs

Marcus Bredt/ARTUR IMAGES
Fotolia Bildagentur
Fuchs Lubritech GmbH
istock Bildagentur
Remmers Baustofftechnik GmbH

978-3-944138-27-5

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1 GROUNDS AND OBJECTIVE

Concrete release agents are ancillary building aids that are required to ensure that formwork can be easily stripped from concrete elements, leaving surfaces in perfect condition. The concrete release agents used are based on mineral oil or vegetable oils and are modified with additives to optimise their properties. To keep risks for humans and the environment as low as possible, requirements on concrete release agents in regard to safe use of the products as well as their compatibility with the environment have grown.

The goal of this State-of-the-Art Report is to provide information on current trends and developments in the area of concrete release agents. Current European regulations are also taken into account. In addition, a description and classification of the raw materials used in the production of concrete release agents are given.

With this State-of-the-Art Report, Deutsche Bauchemie's member companies hope to contribute in promoting concrete release agents that are friendly to users and the environment.

2 HISTORY AND CURRENT DEVELOPMENT

Starting at the beginning of the 1990s, not only technical requirements but increasingly the environmentally relevant aspects of concrete release agents began to play a role.

This also led to consequences for the individual raw materials used in concrete release agents. Hydrocarbon based ingredients were replaced step by step. Not only that, rapid biological degradability was increasingly demanded.

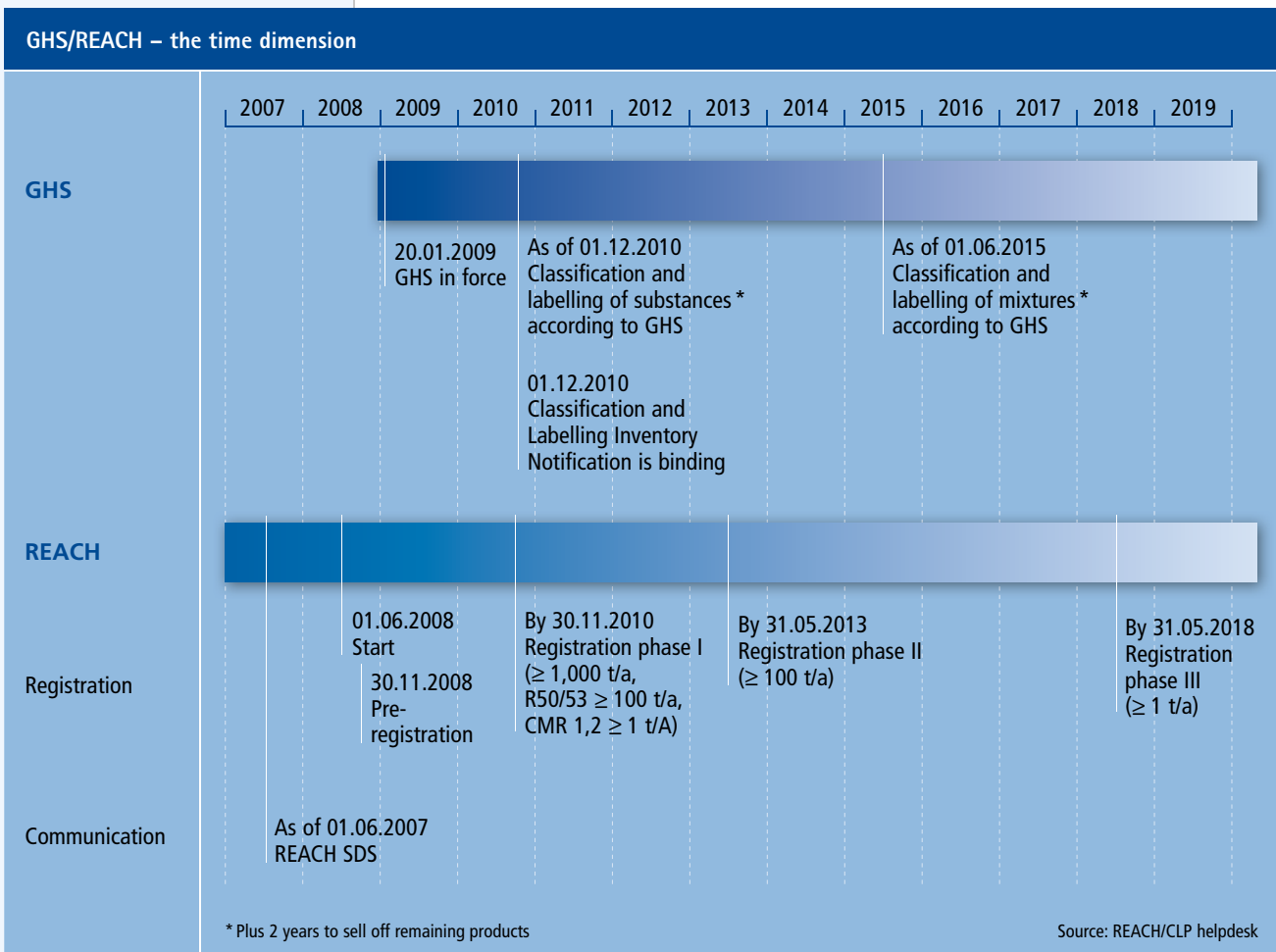
With this background in mind, release agents based on renewable raw materials are increasingly available on the market. These release agents are offered in the form of emulsions and water-free products.

Consumers now find a well-rounded range of concrete release agents at their disposal for all application areas that have been continuously further developed on the basis of experience in practice.

Since June 1, 2007 the new European Chemical Regulation (REACH) has been in force in all of the EU countries. It regulates registration, evaluation and authorisation (approval) of chemicals. With this regulation, a new, uniform law on chemicals is in force in the EU that the concerned companies must implement. The REACH Regulation stipulates that since June 1, 2008, a substance on its own or as an ingredient in a preparation cannot be produced, imported or placed on the market by a company in quantities of more than one tonne per year if the substance has not been registered first. However, there are also substances that are excluded from mandatory registration.



The REACH Regulation has scheduled phase-in deadlines for registration (see Illustration). To benefit from these phase-in deadlines, each manufacturer/importer had to pre-register his REACH relevant substances by November 30, 2010. The last date possible for registering substances produced in quantities between 1 and 100 tonnes is May 31, 2018.



To implement the REACH Regulation, the EU founded the European Chemicals Agency, short ECHA, with headquarters in Helsinki.

As a rule, the manufacturers of concrete release agents belong to the group of downstream users since concrete release agents are usually formulations.

In turn, the raw material supplier must be informed on how his raw materials are used. This information is needed to assess possible risks for humans and the environment and are communicated in the form of an extended Safety Data Sheet. In the end, all of this information will benefit the final user, enabling him to handle the final product safely.



After the REACH Regulation, the GHS Regulation created by the United Nations and its implementation through the European CLP Regulation is the second great change in European legislation on chemicals within a short period of time. Regulation (EC) No. 1272/2008 of the European Parliament and Council went into force on January 20, 2009.

The objective of the regulation is to ensure a high level of protection for human health and the environment and to guarantee the free movement of chemical substances, mixtures and certain specific products within the common European market. The world-wide harmonisation of rules for the classification and labelling of substances and mixtures (GHS created by the UN) for placement on the market and use, on the one hand, and for transport on the other, should not only protect human life and the environment but also facilitate world-wide trade.

The new regulation has been applicable since it went into force on January 20, 2009. After this date, classification, labelling and packaging of substances took place according to Directive 67/548/EEC (dangerous substances directive) until December 1, 2010 and will be implemented for mixtures on June 1, 2015 according to Directive 1999/45/EC (dangerous preparations directive). Classification, labelling and packaging of preparations can take place before June 1, 2015 according to the rules set out in the GHS Regulation, of course, however, the provisions of the dangerous preparations directive are not applicable in this case.

The purpose of the regulation is to identify dangerous chemicals and inform their users on the respective risks with the aid of symbols and statements on packaging labels and with the aid of Safety Data Sheets.

In this conjunction, danger symbols (also called pictograms) were harmonised world-wide.

The well-known Risk and Safety phrases (R/S phrases) will be replaced by H and P statements by June 2015 at the latest.

The [UNECE website](http://www.unece.org) shows what the new symbols look like.

Source: REACH CLP helpdesk

(<http://www.reach-clp-biozid-helpdesk.de/de/Startseite.html>)



3 APPLICATION

Regardless of the raw materials they are based on, concrete release agents must fulfil different requirements. These include concrete technology functions, application properties and occupational health and safety requirements.

3.1 Types of Concrete Release Agents

3.1.1 Concrete Release Agents on a Mineral Oil Base

Concrete release agents on a mineral oil base are mainly used in the construction industry.

Solvent-free concrete release agents on a mineral oil base belong to the group of release agents with the greatest significance on the market for in-situ concrete construction. The products found on the market are good to very good at meeting application and concrete technology requirements.

Solvent-based release agents on a mineral oil base, which must not only achieve the usual functions of concrete technology but also provide outstanding performance when producing fair-faced concrete surfaces in horizontal applications, are mainly used in the pre-fab industry.

Aqueous emulsions and emulsion concentrates based on mineral oil are predominately used for absorbent timber formwork. Their stability as well as shelf-life and sensitivity to frost must be taken into account.

In summary it can be said that release agents on a mineral oil base have reached a high state of development and in conjunction with the large variety of types available, practically any formwork task in the building trade can be solved by a release agent on a mineral oil base.

3.1.2 Concrete Release Agents Based on Renewable Raw Materials

Up until a few years ago, release agents based on renewable raw materials were mainly used as an alternative to mineral oil based concrete release agents for ecological reasons. Meanwhile, the trend to assess the sustainability of products used for construction, including concrete release agents, has increased demand for products with a favourable evaluation. At the same time, what is offered on the raw material side has expanded during the last years due to wide-spread use of vegetable oil esters in the area of fuels. This has given manufacturers of concrete release agents better options for formulating products which can be offered at normal market conditions.





In principle, products on a renewable raw material base are made of refined vegetable oils, vegetable oil esters and sometimes fatty alcohols. Because of the polar structure of the ingredients, they are especially easy to emulsify, the reason most of the release agents in emulsion form found on the market are made of renewable raw materials.

As far as their technological properties are concerned, experience with these release agents has been very good. When carefully applied, fair-faced concrete of outstanding quality can be produced.

Concrete release agents on a renewable raw material base, particularly emulsion products, are predominately used in prefabrication plants.

3.2 Concrete Technology Functions

The goal of using any concrete release agent is to ensure that the stripping process is easy and without difficulties even at different temperatures. The release agent should have no influence on the setting of the concrete (heavy powdering, sanding). Disturbances in the edge zone of the concrete that could reduce compressive strength or, if coatings are to be subsequently applied, reduce adhesion, must be avoided. The concrete release agent should not influence the uniform colouring of the concrete (clouding) and should prevent the formation of pores and pipes as far as possible. It should also protect the formwork from the influence of weather so that the quality of the surface of the concrete will not suffer negative consequences (e.g. excretion of wood sugar, rust, rot, drying out).

3.3 Application-Oriented Requirements

Concrete release agents must be applied in a uniformly closed and thin layer, as a rule, so that they fulfil the technological functions listed above. Application must be easy, economical and possible in different weather conditions. No residue from the concrete release agent should build up on the formwork and the time and expense for cleaning the formwork should be as low as possible. The concrete release agent film on the prepared formwork must be resistant to the influences of weather and should have little tendency to soil before the concrete is placed. Packaged concrete release agents should also have a long shelf-life. Emulsions should remain stable over a sufficient temperature range and not separate. Emulsion concentrates should be easily mixed in the required concentrations.

3.4 Notes on Use

Concrete release agents are used differently and their use is determined by the type of release agent and the type of formwork. When applying, the directions given by the manufacturer such as application method, quantity and formwork substrate should be observed. Normally, ready to use products are used. Emulsion concentrates are diluted with water on site. Particularly in fair-faced concrete areas, formwork substrates should be clean and dry when concrete release agents are applied to prevent the surface of the concrete from becoming soiled. Application techniques are stipulated in the manufacturer's directions and there are different application methods, depending on the viscosity of the concrete release agent. In many cases, thin-liquid products are used which ensure an even and thin film of release agent when applied with high pressure spraying equipment. For special applications there are also highly viscous products (pastes and waxes). Application varies and is determined by the size and type of the formwork and the concrete release agent. Release agents can be applied using high pressure equipment, automatic spraying facilities, rubber wipers, brushes, mops or rags.

Build-up of release agent on formwork can lead to an increased number of pores, sanding, powdering and spotting on the surface of the concrete. Too little release agent can cause the concrete to stick to the formwork which disturbs the surface of the concrete.

The waiting times to be observed after the release agent has been applied, which is particularly important for solvent based products and emulsions, are found in the information supplied by the manufacturer.

Certain concrete release agents based on renewable raw materials must be applied with special care to avoid a water repelling effect on the surface of the concrete. Information on the suitability of the concrete release agent for the different types of formwork (e.g. wood, steel, plastic, concrete) and loads (e.g. mechanical and thermal loads) is given by the manufacturer as well. Further information is also found in the Deutsche Bauchemie publications, "Concrete Release Agents – Information Pamphlet for Users" and in the Code of Practice "Industrial Equipment and Devices for Storing and Applying Concrete Release Agents".



4 ENVIRONMENTAL ASPECTS

Because of the ingredients used, concrete release agents fall under areas that are governed by regulations concerning the environment and occupational health and safety. Along with the mandatory statements on safe handling, storage and disposal of concrete release agents, legislation covering dangerous substances, regulations on the transport of dangerous goods and biodegradability must be taken into account as well.

4.1 Occupational Health/Safety

When using concrete release agents, contact with skin should be avoided by wearing suitable work clothes and oil resistant, protective gloves. Soiled clothing should be changed and cleaned. Concrete release agents should never be sprayed against the direction of the wind or overhead. This can easily be achieved by using proper equipment when working, e.g. an extension pipe for spraying. Care of skin is important and the use of fat based skin creams is recommended. If these simple recommendations for skin protection are not followed, repeated skin contact may cause allergies and skin irritation because release agents dissolve the skin's natural oils. Particularly in concrete construction, these problems are accelerated by the alkaline reaction of cement or concrete in contact with skin. Release agents splashed into eyes can cause irritation, so protective glasses should always be worn.

Along with general hygiene measures, there are also a number of technical and organisational precautionary measures to be taken:

- Ensure ventilation with fresh air when working in interior spaces.
- Keep away from sources of ignition (also electrical equipment without explosion protection), do not smoke and avoid open flames (especially with solvent based release agents)!
- Keep containers tightly closed.
- Make sure a place for washing is close by.
- Keep an eye-bath or eye rinsing bottle handy.

Observance of Code of Practice D 170 Concrete Release Agents issued by the [German] statutory accident insurance organisation for the construction industry (BG Bau) is recommended.

When using concrete release agents in closed spaces, high concentrations of hydrocarbon vapours may occur under certain circumstances caused by solvent vapours or sprayed mist. The employer is responsible for carrying out a risk analysis and, based on the results, implementing appropriate measures (e.g. preparation of a documented procedure).

A differentiated classification of concrete release agent types according to legislation on hazardous substances in GISCODES was undertaken by GISBAU in coordination with Deutsche Bauchemie e.V. There is a code of practice with information on the product including properties and possible hazard potentials for each GISCODE.

After the new GHS Regulation was introduced, classification of the product code (CRA) changed for many concrete release agents because of their viscosity.



BG BAU
Berufsgenossenschaft
der Bauwirtschaft

Startseite » Baustoffe/Markthelfer » Baustoffe » Arbeitssicherheit » D 170

Betontrennmittel

Was ist neu?
Informationen für Ihr Gewerk
Gefährdungsbeurteilung
Hinweis zu Fachinfos
Baustoffe/Markthelfer
Baustoffe
• Allgemein
• Arbeitsschutz
• Persönliche
Schutzmaßnahmen
• Arbeitsverfahren
• 3D-Grundlagen
• Formulare
• Tabellen
• Gesundheitsschutz
Baustoff-Ordner
Baustoff-Markthelfer
Planungs-Informationen
Vorschriften/Regeln
Arbeitsblätter/Formulare
Weitere Medien

Als Betontrennmittel werden folgende Produkte angeboten:
Minerale, Pflanzenöle, Emulsionen, Waxes, Pasten, Lacke

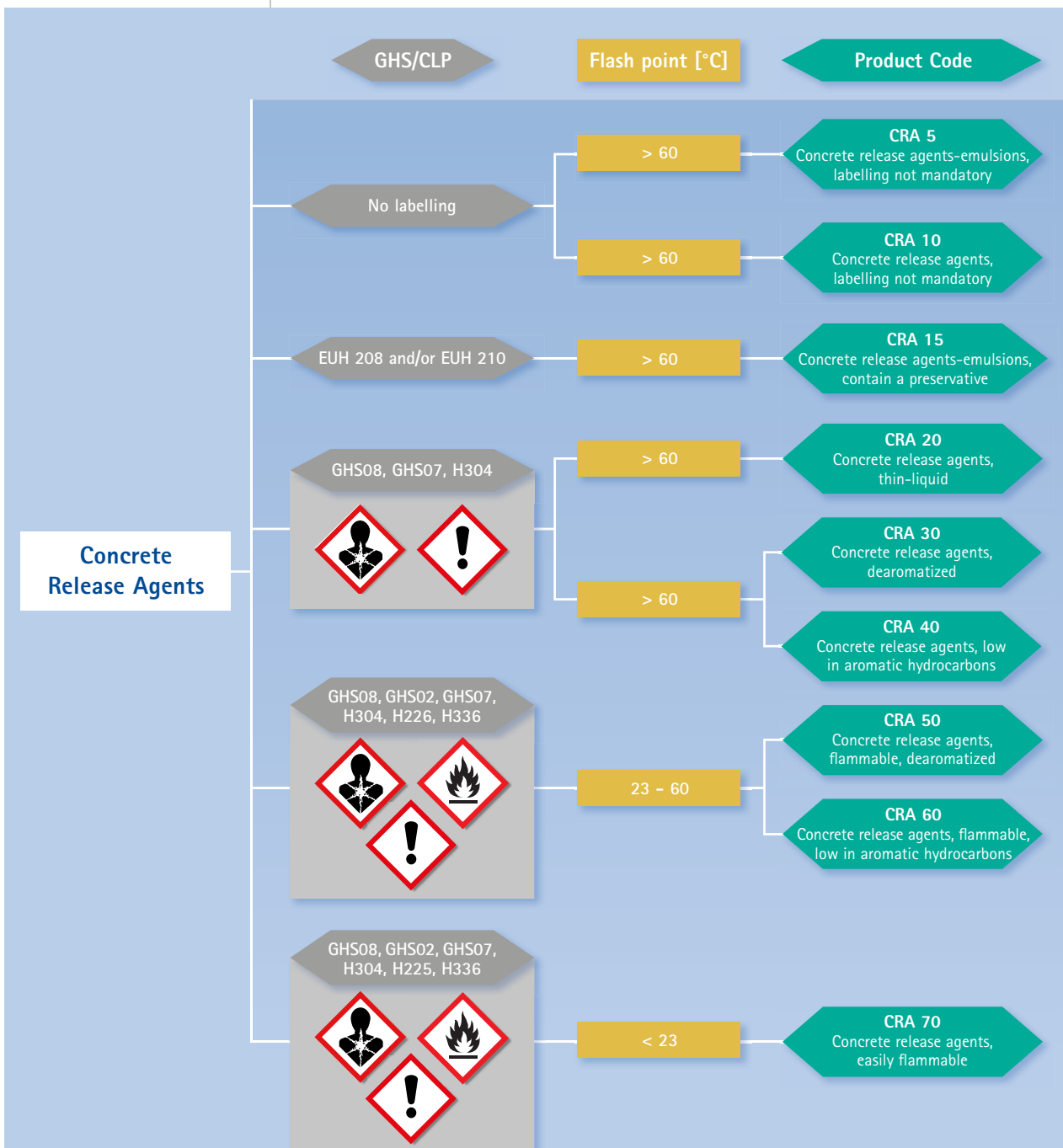
- Betontrennmittel dünn und sparsam auftragen. Beim Aufsprühen Verlängerungsrohr verwenden, um das Erhitzen von Spritzdüse zu begrenzen.
- Zündquellen fernhalten, offene Flammen vermeiden.
- Vorklammern am Arbeitsort auf Schweißbedarf beschränken.
- Gefäße geschlossen halten.
- Beim Verarbeiten in Räumen, Lüftungsmaßnahmen durchführen (Fenster und Türen öffnen).
- Bei lösemittelhaltigen Produkten Atemschutz mit Kombifiltern A2-P2 benutzen, wenn Lüftungsmaßnahmen nicht ausreichen und Temperaturdehng und -nebel angefallen werden können.
Bei lösemittelhaltigen Produkten Partikelfilter P2 bzw. FFP2 benutzen (bei Spritzverfahren).
- Unbedeckte Körperpartie mit fetthaltiger Hautschutzsalbe eincremen.
- Geeignete Körpereschutzmittel benutzen, z. B. Gesichtsschutz, Schutzbrille, Schutzhandschuhe aus Nitril oder Butylkautschuk.
- Bei Spritzern in die Augen sofort mit viel Wasser spülen und umgehend den Augenarzt aufsuchen.

Vorsorgeuntersuchungen
Arbeitsmedizinische Vorsorgeuntersuchungen nach Ergebnis der Gefährdungsbeurteilung vorselektieren (Pflichtuntersuchungen) oder anbieten (Angebotsuntersuchungen). Hierzu Beratung durch den Betriebsarzt.

On December 1, 2010 the viscosity limit for mineral oils in regard to labelling increased from $< 7 \text{ mm}^2/\text{s}$ to $\leq 20.5 \text{ mm}^2/\text{s}$, determined at $40 \text{ }^\circ\text{C}$. Due to increasing acceptance on the market, a new product group, CRA 5, was introduced for concrete release agent emulsions that do not require labelling. The product group codes were aligned with the current CLP Regulation. That is why practically all products on a mineral oil base no longer fall under product code CRA 10 but are now classified in CRA 20. As of June 1, 2015, this applies for concrete release agents with a mineral oil content as of $\geq 10.0 \%$. [25]

According to an assessment made by the manufacturers organised in Deutsche Bauchemie e.V., most release agents are assigned to CRA 10, CRA 15, CRA 20, CRA 30 and CRA 50.

Diagram of "Product Groups Concrete Release Agents"

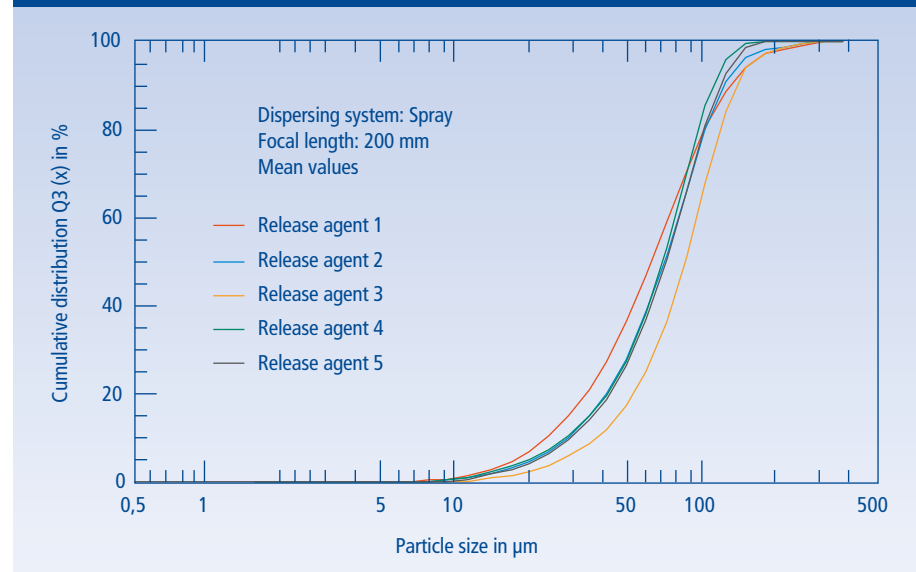




When spraying equipment is used to apply concrete release agents, "sprayed mist" (aerosols) form. Aerosols with a particle size less than 10 μm are defined in specialist medical literature as being capable of passing into the lungs. Aerosol particles with a diameter $< 5 \mu\text{m}$ can reach and be deposited in the peripheral bronchial tree (alveoli) while particles with a diameter between 5 μm and 10 μm are deposited in the upper respiratory tract and central bronchial tree. To answer the question whether spraying concrete release agents produces particles in the sprayed mist that can penetrate into the alveoli, examinations were commissioned by Deutsche Bauchemie e.V. to determine the particle size distribution of the resulting droplets. Five different mineral oil based concrete release agents were tested.

To be able to give a general statement on the concrete release agents found on the market, solvent based as well as solvent-free products were selected. Spraying was carried out with a type of hand spray gun normally used in practice, using a very fine, flat spray nozzle and an operating pressure of 5 bar. The determination of particle size distribution by means of a laser diffraction method showed that the sprayed mist did not contain an appreciable number of particles $< 5 \mu\text{m}$ under the stated examination conditions. Even in the range between 5 μm and 10 μm relevant for answering the question, the figure determined was clearly below one percent.

Illustration: Particle size distribution of release agents (excerpt from Analysis Report [15])



The results prove that when concrete release agents are sprayed properly the resulting mist will not pass into the lungs.

4.2 Transport/Storage

The transport and storage of concrete release agents takes place in tightly closed containers. If a leak occurs, liquid concrete release agents could penetrate unhindered into the ground and thus also mix with water, regardless of whether the water is in the ground or on the surface. The general Administrative Regulation (VwVwS) of the German Water Management Act (WHG) assesses substances that could have a long-term negative effect on the physical, chemical or biological state of water. Depending on their properties, they are classified in Germany as not hazardous to water (nwg) or in one of the Water Hazard Classes (WGK):

nwg: not hazard to water

WGK 1: Low hazard to water

WGK 2: Hazard to waters

WGK 3: Severe hazard to waters

Evaluation of the water hazard potential is carried out based on the properties of the substances, particularly acute toxicity to mammals (oral and/or dermal), toxicity to aquatic organisms (usually fish and bacteria), biological degradability as well as potential for bioaccumulation by the Commission for the Evaluation of Water Hazardous Substances (KBwS) in which the German Federal Government, States and industry are represented.

As a rule, concrete release agents are preparations that contain water hazardous substances. The classification of substance mixtures is described in VwVwS. According to VwVwS rules, manufacturers of concrete release agents can take responsibility for assessing the water hazard class themselves.

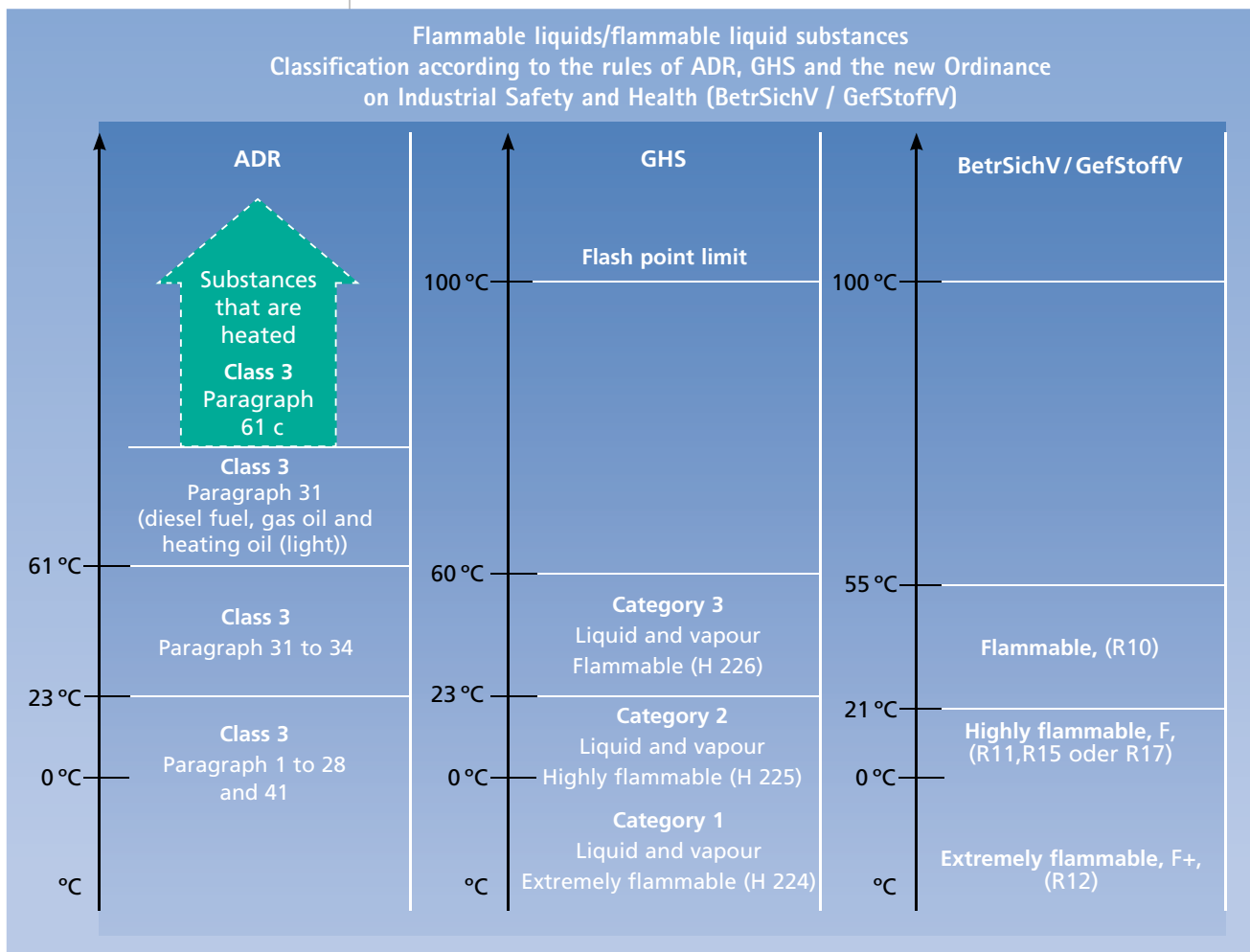
Equipment and devices for storing, filling and handling water hazardous substances are subject to legal requirements that depend on the hazard potential of the equipment and devices. The requirements arise from the water hazard class and the quantity of the water hazardous substances (see regulations for each specific State).

Moreover, the Ordinance on Industrial Safety and Health (BetrSichV) applies in which the employer is obligated to carry out a risk analysis for each raw material used with the help of the CLP Regulation and the general principles of health and safety and to implement precautionary measures based on the results of this.



According to a European agreement concerning the international carriage of dangerous goods by road, air and inland waters, the transport of concrete release agents is governed by ADR (01.01.2011). Carriage by sea is governed by its own regulation (GGVSee).

A concrete release agent is deemed a dangerous good if its flash point exceeds the specified limit or it poses a risk to the environment. The potential for risk thus lies in the use of solvents with low flash points (< 61 °C) or substances that are hazardous to the environment.



4.3 Disposal

Leftover concrete release agents are oily substances, regardless of the raw material they are based on. Leftovers must be separately disposed of and should not be mixed with other substances. Particular attention should be paid that leftovers are not allowed to penetrate into the ground or come in contact with ground or surface water.

Residue that remains on formwork is of no concern when it comes to disposal because of the insignificant quantities involved.

Completely empty containers should be recycled according to the Packaging Waste Regulation (VerpackV). Packaging bears the license mark of the disposal industry. Information on disposal is found in the Safety Data Sheets that are issued by the manufacturer.

4.4 Biological Degradability

If a concrete release agent reaches the environment, it has a negative effect on the eco-system. In the case of concrete release agents, attention is usually paid to their influence on an aquatic eco-system by determining their biodegradability. Biodegradability is divided into readily and inherently biodegradable and biodegradable in principle. Biological degradation is the chemical conversion of organic substances by micro-organisms all the way to mineralization and/or the formation of biomass in aquatic environments. There is a specific test method for each stage. A concrete release agent that is readily biodegradable has the least adverse effect on the eco-system.

The determination of rapid biodegradability is carried out according to OECD Guideline 301. The deciding factor here is the degree of biodegradability in a so-called 10-day time frame. Since not every test is suitable for the examination of products that contain oil, a test method should be selected from among the possible OECD 301 A-F tests that is appropriate for the composition of the product.

BOD – biological oxygen demand
CO₂ – carbon dioxide development
COD – chemical oxygen demand
DOC – dissolved organic carbon

Test method	Parameter	Duration (days)	Limit value (%)	OECD Guideline
Readily biodegradable				
DOC Die Away Test	DOC	28	70	310A
CO ₂ Evolution Test	CO ₂	28	60	301B
Closed Bottle Test	BOD	28	60	301D
Manometric Respirometry Test	BOD	28	60	301F
mod. MITI (I) Test	BOD	28	60	301C
mod. OECD Screening Test	DOC	28	70	301E
Inherently biodegradable				
Zahn-Wellens/EMPA-Test	DOC/COD	28	20	302B
mod. SCAS Test	DOC	variable	20	302A
mod. MITI (II) Test	BOD	28	20	302C
Biodegradable in principle				
Simulations Test	DOC	3-6 weeks		303A

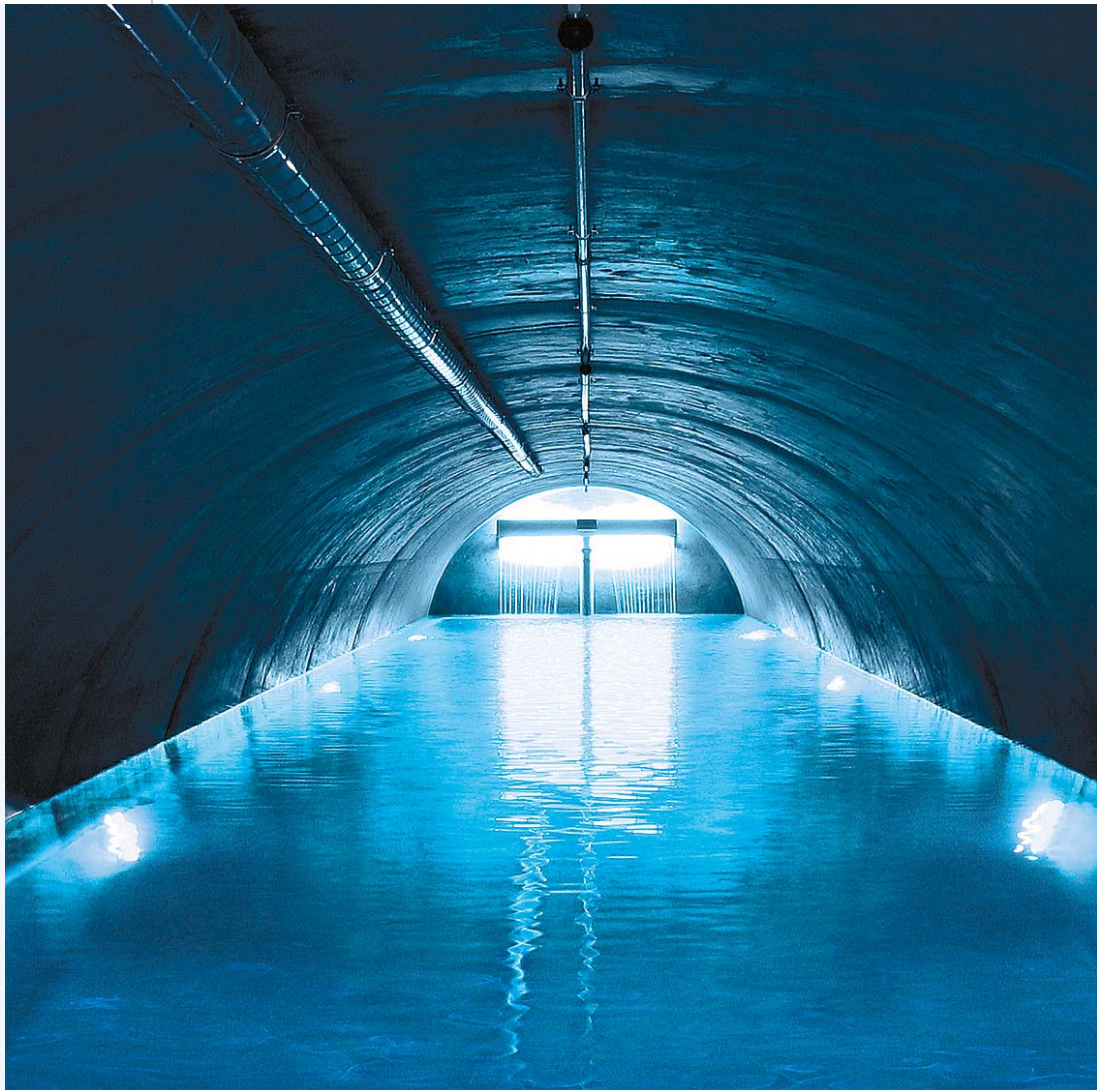
As a rule, concrete release agents on a mineral oil base are inherently (potentially) biodegradable or biodegradable in principle; those based on renewable raw materials are usually readily degradable. It is now being observed that with increasing environmental awareness, the demand for readily biodegradable products based on renewable raw materials continues to grow.

It is also still possible that the release agent can be marked with the "Blue Angel" eco-label. To receive this mark, the requirements set out in RAL-UZ 178 must be fulfilled.

4.5 Use in Drinking Water Areas

According to § 17 of the German Drinking Water Ordinance, linings that come in contact with drinking water can only be made of materials that do not give off substances in concentrations higher than unavoidable according to the state-of-the-art, do not compromise protection of human health or change the odour or taste of the water they come in contact with. Work Sheet W 347 issued by the German Technical and Scientific Association for Gas and Water (DVGW) defines the hygienic requirements and tests for cement bound working materials, admixtures, additives, and ancillary materials which includes concrete release agents.

Concrete release agents must not only be subjected to a micro-biological test in accordance with DVGW Work Sheet W 270 but also to migration tests (e.g. odour, cloudiness, release of TOC and heavy metals). In addition, their ingredients must be listed in the Positive List (Annex A) enclosed with Work Sheet W 347.





4.6 European Classification Systems for Evaluation of Concrete Release Agents

In most European countries there is no special classification system for concrete release agents. Instead, the systems already in place cover all products used for construction.



In Sweden for example, the BASTA System is used with the intention of eliminating construction products that contain dangerous substances. Suppliers can register their products, e.g. including concrete release agents, if certain requirements are met. The evaluation criteria for the composition of the product is oriented to the CLP implementing regulation of the European Community.

In France and the Netherlands, classification systems especially for concrete release agents were created by the responsible trade associations to increase transparency and comparability of the products found on the market in regard to their environmental properties.

The French Association of Concrete and Mortar Additive Manufacturers (SYNAD) revised its classification for concrete release agents in 2010. The most important suppliers of construction chemical products on the French market are organised in SYNAD. Concrete release agents are divided into groups according to substance properties (vegetable/mineral oil base). Within the groups, the products are assessed according to the criteria fire hazards, hygiene and health protection at work, VOC content and biodegradability according to OECD 301F. Symbols of one to five water drops are awarded. Concrete release agents based on vegetable oils are awarded a quality mark in the form of a clover leaf (Appellation Végétal).



The 10-years of experience with Classification SYNAD has shown that the spread and acceptance of concrete release agents on a vegetable oil base have gained momentum on the French market.

The Dutch Association of Concrete Release Agent Manufacturers (Stichting Beton Losmiddel Fabrikanten) in cooperation with public health authorities already had a classification system in place in 1998. Organised in the association are 5 suppliers of concrete release agents which cover approx. 85 % of the Dutch market. The products are divided into five classes, differentiated according to biodegradability and labelled according to the CLP Regulation. Release agents that are mainly produced from renewable raw materials and readily biodegradable according to OECD 301 as well as free of solvents are assigned to the highest class. On the Dutch market as well, classification by BLF has successfully promoted the acceptance and spread of release agents made of renewable raw materials. However, classification has not been updated since it was introduced by SBLF.

5 RAW MATERIALS

5.1 Main Ingredients

5.1.1 Mineral Oils (Paraffin and Naphthene Based)

Mineral oils are complex substance mixtures consisting of paraffin, naphthene and aromatic hydrocarbons with medium length chains. As a rule, the mineral oils used in concrete release agents are highly hydrogenated so that the content of aromatic hydrocarbons can be kept very low. The flash point of the mineral oils used is clearly above 100 °C.

Composition is essentially determined by origin. Natural sources with naphthene as the main constituent are found predominately in Argentina and Venezuela. Natural sources with paraffin as the main constituent are wide-spread. The oils used for concrete release agents are won by fractional distillation or by cracking (cracking of large molecules) and hydrogenation. Mineral oils are used in concrete release agents as a carrier or base raw material and they separate the concrete from the formwork through physical conditions (hydrophobic effect of oil to water).

Naphthene and paraffin based mineral oils are not dangerous substances within the meaning of the CLP Regulation provided that kinematic viscosity is greater than 20.5 mm²/s at 40 °C and the PCA content is below 3 %.

5.1.2 Synthetic Oils

Synthetic oils are high quality base oils that are produced with defined chemical and physical properties and are suitable for the most various application areas.

These are won as paraffin based base oils by hydrocracking long-chained paraffins (slack wax). The unsaturated compounds present in the form of impurities are hydrogenated by enriching with hydrogen. Synthetic oils are used in release agents as carrier liquids for additives.

Synthetic oils are not hazardous substances within the meaning of the CLP Regulation as long as kinematic viscosity is greater than 20.5 mm²/s at 40 °C and the PCA content is below 3 %.



5.1.3 Gas Oils

A new raw material base for the production of release agents are hydrocarbons that are produced according to the GTL process (gas-to-liquids). With the GTL process, natural gas becomes a synthesis gas through the addition of oxygen and hydrogen and is then converted in a Fischer Tropsch synthesis to hydrocarbon mixtures.

This new raw material base is completely sulphur-free and does not contain any aromatic compounds or organic nitrogen. PCA contents are extremely low and range in total < 1 ppm.

This new raw material has no colour or odour. Labelling takes place according to the same rules for mineral and synthetic oils.

5.1.4 Vegetable Oils

Vegetable oils are oils based on renewable raw materials (rapeseed, soybean, coconut, palm kernel, sunflower seed oil, etc.). From a chemical standpoint, these are triglycerides of natural fatty acids.

Vegetable oils are won by cultivating the plants named above. In release agents, vegetable oils are used as a carrier or base raw material. They achieve separation by a chemical/physical effect.

Rapeseed and sunflower seed oils are not water hazardous substances as a rule. The vegetable oils used for concrete release agents are not toxic and there is no classification according to the CLP Regulation.

5.1.5 Fatty Acid Esters

Fatty acid esters are won directly (e.g. from rapeseed oil) but also increasingly through esterification or interesterification of natural resources. They are used in the lubricant and food industries. In concrete release agents on a mineral oil basis, fatty acid esters are used as an additive. Depending on the type of ester, they mainly have the function of reducing pores or of improving release properties. In mineral oil-free release agents, fatty acid esters are used not only as an additive for the reasons given above but also as base oils because of the favourable ecological properties of fatty acid esters.

Certain esters from dietary fatty acids are permitted for use as foods additives (e.g. E 491– 495). These are readily biodegradable. Only fatty acid esters with an even numbered, unbranched carbon chain with 12 or more carbon atoms, either with a fatty acid or a fatty alcohol side group, are not substances hazardous to water; the remaining fatty acid esters are WGK 1.





5.1.6 Waxes

Wax is a technological umbrella term for a number of naturally and synthetically won substances with the following properties:

- Melts at temperatures above 40 °C without decomposition
- Has relatively low viscosity just above the melting point
- Consistence and solubility are highly dependent on temperature

Depending on origin, waxes are divided into natural waxes (e.g. vegetable waxes, animal waxes and mineral waxes), chemically modified waxes and synthetic waxes (e.g. hard waxes). They can be used for numerous applications. In concrete release agents they are used as base substances but also as additives to improve the properties of the release film.

As a rule, waxes are either substances that are not hazardous to water or they are classified Water Hazard Class 1.

5.1.7 Paraffinic Solvents



The solvents used in concrete release agents are paraffin based, thin-liquid, volatile and complex hydrocarbon mixtures. In release agent areas, de-aromatised hydrocarbons are preferably used. Compared to mineral oils, the viscosities of solvents lie clearly below 2 mm²/s.

Solvents for release agents, defined by fractions, are won by hydrogenating petroleum fractions and by hydrocracking. They are used in release agents to control viscosity and the thickness of the release film and also as a carrier liquid for additives – also mixed with other higher viscous oils. In addition, this class of substances has very good spreading (creep) behaviour on formwork. After the release agent is applied, the solvent evaporates at a defined rate.

Paraffin based, de-aromatised solvents are assigned to Water Hazard Class 1. Solvents must always be labelled according to the CLP Regulation.

5.2 Additives

5.2.1 Fatty Acids

This term is generally understood as unbranched carboxylic acids. Typical representatives are those of natural origin with 12 to 22 carbon atoms. Fatty acids are won by cracking vegetable oils and animal fats. They are very weak acids and are used as starting products for surface-active agents, lubricants, cosmetics and food. In concrete release agents, mixtures of long-chain fatty acids (e.g. stearic acid and oleic acid) in particular are used. They function by a chemical release effect in which they convert constituents in the fresh concrete on the surface of the concrete into water insoluble metallic soaps. This reaction increases the physical release effect.

Edible fatty acids (E 570) are permitted as food additives and are readily biodegradable. Fatty acids with saturated, unbranched and even-numbered carbon chains with 14 or more carbon atoms are not water hazardous substances. Other fatty acids are assigned to Water Hazard Class 1.

5.2.2 Fatty Alcohols

Fatty alcohols are generally understood as linear, saturated or unsaturated primary alcohols with 6 to 22 carbon atoms. They are mainly produced from natural fats and fatty acids through catalytic reduction. They are neutral, oily to paste-form liquids that are used as raw materials for surface-active agents as well as for creams and ointments. Long-chain fatty alcohols are used as a base oil in concrete release agents because of their favourable ecological properties.

Saturated fatty alcohols with 14 and more carbon atoms and an even-numbered carbon chain as well as unsaturated fatty acids with 16 and 18 carbon atoms and even-numbered, unbranched chains are readily biodegradable as a rule and belong to the group of substances that are not hazardous to water.

5.2.3 Resins

The resins used in release agents are natural, solid or semi-liquid, organic substances that are composed of different chemical substances. After drying, most resins form continuous films from solutions or emulsions.

Natural resins are predominately won from exudates from certain trees (resin balsam). In the concrete release agent area, natural resins are mainly used for formwork varnishes. Colophony types are the ingredients most often used for effective separation.

The resins used are practically insoluble in water and are mainly classified WGK 2.

In rare cases, there may be sensitising effects which makes labelling according to the CLP Regulation necessary.

5.2.4 Emulsifiers (Surface-Active Agents)

Emulsifiers are so-called interface-active substances. This is the term used for chemical compounds that strongly concentrate at interfaces out of solution and in doing so reduce interfacial tension. This allows liquids that do not normally mix (e.g. oil/water) to be mixed, i.e. an emulsion results. So in this case a surface-active agent acts as an emulsifier.

The number of available types of surface-active agents is very large. Surface-active agents may be natural, partially synthetic or entirely synthetic in origin. In addition, they can also be divided into activity classes: anionic surface-active agents, cationic surface-active agents, non-ionic surface-active agents and amphoteric surface-active





agents. The range of use of surface-active agents or emulsifiers is extremely varied and they are essential for formulating release emulsions. In non-aqueous release agents they are used as spreading agents and as additives to suppress pores on the surface of the concrete. In the release agent area, fatty acid esters (ethoxylated and non-ethoxylated), fatty alcohols and fatty amine ethoxylates are usually used.

Most of the surface-active agents do have a long-term harmful effect on aquatic organisms which results in a classification of Water Hazard Class 2. However, some surface-active agents fall under Water Hazard Class 1. Practically all of the surface-active agents used in release agents are readily biodegradable.

Most of the products used must be labelled according to the CLP Regulation.

5.2.5 Corrosion Inhibitors

Corrosion inhibitors are products that provide passive protection against corrosion and are used to protect devices and equipment from attack by corrosive mediums.

Typical corrosion inhibitors in release agents are calcium sulphonates, succinic acid half-esters, fatty amines or imidazoline compounds. They are used in release agents to temporarily prevent rust on steel formwork.

The corrosion inhibitors used in release agents are classified Water Hazard Class 1 or 2 as a rule. They are at least inherently biodegradable and, in some cases, readily biodegradable.

Most of the products used must be labelled according to the CLP Regulation.

5.2.6 Biocides

When producing release agent emulsions, a biocide must be used as a preservative to protect the water based emulsions from bacteria, yeast and fungi.

The preservative as well as the active ingredients in the preservative are subject to the provisions and rules set out in the European Biocides Regulation (BPR).

Depending on the type of emulsion, the quantities used range between 0.05 -1.0 % related to the total formulation.

Today, several important biocidal ingredients are already classified as sensitising as of a certain quantity. Due to the CLP Regulation, the criteria for additional labelling of mixtures that contain sensitising substances in low concentrations will change. As of June 1, 2015, it may be necessary to additionally label release agent emulsions with the EUH statement 208 "Contains (name of sensitising substance), may cause allergic reactions".

6 SUMMARY

In the fourth edition of this State-of-the-Art Report, the effects of the new rules of the European chemicals legislation concerning concrete release agents and their raw materials are described. The State-of-the-Art Report therefore also provides an overview of current trends and developments in a European context.

Today users find a well-rounded range of concrete release agents on the market for all application areas. Mineral oil based products are still the most commonly used products. Especially in pre-fabrication plants, emulsions have become established as technically practical and environment-friendly alternatives and have gained a significant share of the market (> 10 %). The most important aspects concerning application and use are briefly presented. More detailed information on this is found in the brochures published by Deutsche Bauchemie, "Concrete Release Agents – Information Pamphlet for Users" [29] and the Code of Practice "Industrial Equipment and Devices for Storing and Applying Concrete Release Agents" [30].

As of June 1, 2015, the CLP Regulation of the EU, which has been in force since 2009, will also apply to preparations such as concrete release agents. For a large number of existing mineral oil based products, labelling will become necessary because the viscosity limit will change as of this date. Products labelled as such must then be classified as aspiration toxic (H 304). Concrete release agents that are formulated exclusively on renewable raw materials are not affected. A differentiated classification in compliance with legislation on hazardous substances into GISCODES was carried out by GISBAU in cooperation with Deutsche Bauchemie.

The new European chemical regulation (REACH) also applies to the raw materials used in concrete release agents. Most of these have meanwhile been registered by suppliers.

Biodegradability is differentiated between readily biodegradable, inherently biodegradable and biodegradable in principle. To determine biological degradation, Deutsche Bauchemie recommends testing the entire formulation, using one of the OECD methods since with these methods all of the ingredients in the formulation are evaluated. It makes no difference whether the product is an emulsion or an oily preparation. Release agents made of renewable raw materials are readily biodegradable as a rule; those on a mineral oil base as a rule inherently biodegradable or biodegradable in principle.

Concrete release agents can also be used for concrete building elements that come in contact with drinking water. These release agents must comply with the requirements in Work Sheet W 347 issued by the German Technical and Scientific Association for Gas and Water (DVGW), "Hygiene Requirements for Cement-Bound Working Materials in Drinking Water Areas".

The water hazard class of release agents is determined on the basis of the "Administrative Regulation for the classification of water hazardous substances (VwVwS) set out in the [German] Federal Water Act" based on the classifications of the raw materials. Most of the release agents fall under WGK 1. At present, the only release agent preparations that are not hazardous to water are based on unmodified vegetable oils. However, these do not meet concrete technology requirements as a rule.





The classifications for concrete release agents that exist in France and the Netherlands have improved the transparency and comparability of the products on the market in regard to their environmental properties and promoted the share of environmentally compatible products on the market. Other European countries have not followed suit and even EFCA put its initiative to create a European classification system on ice after a brief discussion.

In the second part of this State-of-the-Art Report the most important raw material classes for formulating release agents are described in regard to their environmental behaviour. They are divided into main ingredients and additives.

The mineral and synthetic oils used are usually label-free products in Water Hazard Class 1 that are inherently biodegradable. Because the majority of raw materials have low viscosity, they are subject to labelling according to the CLP Regulation.

The pure vegetable oils used are label-free substances that are not hazardous to water (nwg substances) and readily biodegradable. Vegetable oil derivatives are evaluated similarly although these are classified Water Hazard Class 1.

Solvents for concrete release agents are paraffin based, de-aromatised, inherently biodegradable hydrocarbon mixtures in Water Hazard Class 1 that must be labelled because of their low viscosity and flash point.

The fatty acids, fatty alcohols and fatty acid esters are mainly label-free, readily degradable substances that are assigned to Water Hazard Class 1.

The emulsifiers used in the additive area must be labelled as a rule and are readily degradable substances in Water Hazard Class 2.

Corrosion inhibitors are subject to mandatory labelling which varies depending on composition. They are inherently biodegradable and assigned to Water Hazard Class 1 or 2.

By examining the most important raw materials, a differentiated picture comes to view on the evaluation of concrete release agents in regard to environment relevant criteria. This State-of-the-Art Report aims to enhance transparency on the technology and composition of concrete release agents and take the public's need for information into account.

When the GHS Regulation is applied to concrete release agents, many formulations on a mineral oil base will suddenly become dangerous substances. That makes it necessary for the user to check whether these products cannot be replaced with products that do not need to be labelled. In view of increased awareness of preventive health protection, the companies organised in Deutsche Bauchemie support the imperative of substitution.

7 ANNEX 1: DEFINITION OF TERMS

additive	A substance that is added to other substances or products in small quantities to alter their properties in a certain way.
ADR	Accord européen relatif au transport international des marchandises dangereuses par route (European agreement on international carriage of dangerous goods by road)
aerobic biodegradation	Biological degradation in the presence of oxygen as a reaction partner; the opposite of anaerobic biodegradation (in the absence of oxygen).
aerosol	Air with suspended particles of finely distributed liquids.
AGW	Arbeitsplatzgrenzwert – German occupational exposure limit value is the average concentration of a substance in the air at the workplace at which acute or chronic harm of workers' health is not to be expected.
aliphatic compounds	Class of substances in organic chemistry consisting of straight-chain or more or less branched chains of hydrocarbons.
alkaline reaction	Substances which in the presence of water have a pH value > 7 (excess of hydroxyl ions), pH > 7 - 14 is in the alkaline range.
amphotensides	Surface active agents which have a negatively as well as a positively charged functional group are designated as amphoteric or also zwitterionic surface active agents.
antioxidants	Organic compounds that are added to products such as oils and fats to prevent undesired changes (oxidation, e.g. resinification) or to strongly slow down such changes.
aromatic compounds	Class of substances in organic chemistry, e.g. benzene C ₆ H ₆ and its derivatives. Ring-shaped hydrocarbon compounds with an electron system typical for aromatic compounds.
bacteria toxicity	Toxic effect on bacteria.
BArb.Bl.	Bundesarbeitsblatt – journal published by the German Federal Ministry of Labour and Social Welfare in which official announcements are made
BetrSichV	Betriebssicherheitsverordnung – German Ordinance on Industrial Safety and Health
Blauer Engel	An eco-label that is awarded to products which, when compared to conventional products for the same intended purpose, are more environmentally sound and no less fit for use.
BLF	Stichting Beton Losmiddelen Fabricanten (Dutch Association of Concrete Release Agent Manufacturers)
BPR	Biocidal Products Regulation

BOD	Biological oxygen demand
CHC	Chlorinated hydrocarbons
CLP Regulation	Regulation (EC) No. 1272/2008 (CLP Regulation) on Classification, Labelling and Packaging of Substances and Mixtures
CMR substance	A substance that is carcinogenic (causes cancer), mutagenic (causes mutations) or reprotoxic (toxic to reproduction)
corrosion inhibitors	Additives that prevent the corrosion of metals or strongly inhibit corrosion.
derivatives	A substance or compound obtained from, or regarded as derived from, another substance or compound.
DVGW	Deutscher Verein des Gas- und Wasserfaches e.V. – German Technical and Scientific Association for Gas and Water
ECHA	The European Chemical Agency that monitors implementation of the REACH regulation
Eco-toxicology	Science concerned with the distribution and effects of chemical substances on organisms when direct or indirect harm for the environment and humans is involved.
EFCA	European Federation of Concrete Admixtures Associations
EINECS	European Inventory of Existing Commercial Chemical Substances
emulsifiers	Interface-active substances that stabilise a fine distribution of two liquids that are immiscible (example: oil/water).
emulsion	A system consisting of two liquids that are immiscible in which one of the liquids is dispersed throughout the other.
EUH statement	Supplemental hazard statements (H statements), which have not been taken into account in GHS and are only used in the EU.
fish toxicity	Evaluation of a harmful influence on fish.
flash point	Temperature at which under defined conditions a liquid develops flammable gas mixtures.

form liners	A type of lining for formwork made of liquid plastics that harden on a negative form (or is supplied as serial patterns) which create new possibilities for patterned concrete surfaces.
GHS	Globally Harmonized System (world-wide, uniform system created by the United Nations for classification and labelling chemicals)
GISBAU	Hazardous substance information system issued by the German trade associations in the construction industry
GISCODE	A [German] classification system used in GISBAU to assign product groups according to their risk potential.
H and P statements	Hazard and precautionary statements according to the CLP Regulation
hydratation of cement	Chemical reaction of cement with water resulting in hydrated cement.
hydrophobicity	Water repelling effect
Interesterification	Chemical reaction of an ester with an alcohol in order to obtain a different ester.
MAK value	German maximum workplace concentration; the highest permissible concentration of a substance in the air at the workplace as a gas, vapour or suspended particle at the workplace that does not affect worker's health.
mineral oil	Liquid distillation products won from mineral raw materials that essentially consist of mixtures of saturated hydrocarbons.
OECD	Abbreviation for Organisation for Economic Cooperation and Development
oral mammal toxicity	Toxic effect on mammals (e.g. rats) after oral intake (swallowing).
PCA	Polycyclic aromatic hydrocarbons
phase-in substance	A substance that is listed in the European Inventory of Existing Commercial Chemical Substances (EINECS) and has an EINECS number.
pipes	Hollow voids in concrete that result from insufficient compaction or separation of water in the fresh concrete.

RAL UZ 178	Rules for the award of the environment label „readily biodegradable lubricants and formwork oils“ issued by RAL-German Institute for Quality Assurance and Certification (RAL GmbH).
REACH	European Community regulation on registration, assessment and approval of chemical substances called REACH – Registration, Evaluation, Authorisation and Restriction of Chemicals.
SIEF	A forum under REACH for the exchange of information on substances.
SYNAD	Le Syndicat National des Adjuvants pour Bétons et Mortiers (French Association of Release Agent Manufacturers)
TOC	Total Organic Carbon
toxicology	Science on the disturbances on living systems caused by substances, i.e. toxic effects.
TrbF 20	German Technical Rule for Flammable Liquids: storage rooms
TRGS	Technische Regel für Gefahrstoffe – German Technical Rules for Hazardous Substances
UNECE	United Nations Economic Commission for Europe
VwVwS	Verwaltungsvorschrift wassergefährdende Stoffe – German Administrative Regulation for the Classification of Water Hazardous Substances into Water Hazard Classes
Water Hazard Classes (WGK)	<p>Wassergefährdungsklassen – Designation of a German system consisting of three classes to characterise the degree substances are hazardous to water.</p> <p>WGK 1: low hazard to water</p> <p>WGK 2: hazard to water</p> <p>WGK 3: severe hazard to water</p> <p>Substances that are not hazardous to water are designated "nwg" (not hazardous to water) and listed in VwVwS.</p>
WHG	Wasserhaushaltsgesetz – German Federal Water Management Act
Wood sugar excretion	The excretion of substances in wood from the formwork which may take place under certain conditions and has adverse effects on concrete surface quality.

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9 FINAL REMARKS

This fourth, updated edition of the State-of-the-Art Report „Concrete Release Agents and the Environment“ was prepared by Work Group 2.3 “Concrete Release Agents” (AK 2.3) and discussed and adopted by Special Committee 2 “Concrete Technology” (FA 2). The purpose of this State-of-the-Art Report is to provide information to all member companies as well as the interested public. All of the documents submitted by the end of April 2015 as well as the feedback we received concerning the 3rd edition of this State-of-the-Art Report published in June 2008 were integrated into this report.

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Deutsche Bauchemie e.V. would be pleased if you would share your experience regarding this State-of-the-Art Report and invites you to make comments which should be directed to the main office in Frankfurt.





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