Draft Guidance for Annex V

Disclaimer:

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Users are also reminded that this document is a draft guidance which was handed over to the European Chemicals Agency (ECHA) for further development in cooperation with Member States and relevant stakeholders and for subsequent insertion into the Guidance on registration. The Agency has the task of providing technical and scientific guidance and tools for the operation of the Regulation (EC) No 1907/2006 (REACH) under its Article 77(2).

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Article 2(7)(b) of the Regulation (EC) No 1907/2006 (REACH) sets out criteria for exempting substances covered by Annex V of this Regulation from the registration, downstream user and evaluation requirements. These criteria are formulated in a very general way. This guidance is intended to give more explanations and background information for applying the different exemptions and give clarifications when an exemption could be applied and when not. It should be noted that the companies benefiting from an exemption must provide the authorities (on request) with appropriate information to show that their substances qualify for the exemption.

The guidance below follows the same ordering as the entries in Annex V of the REACH regulation.

1. Substances which result from a chemical reaction that occurs incidental to exposure of another substance or article to environmental factors such as air, moisture, microbial organisms or sunlight.

Most substances present a certain level of instability upon exposure to environmental factors such as air, moisture, microbial organisms and the irradiation from sunlight. Any reaction products thus formed do not have to be registered as it would be impractical; they are generated incidentally and without the awareness of the manufacturer or importer of the original substance.

For example, the reaction products from the incidental hydrolysis of substances (e.g. esters, amides, acryl halides, anhydrides, halogenated organosilanes, etc.) in contact with the moisture from the environment are exempted from registration as they fall within this criterion. Another example is diethyl ether which may form peroxides after exposure to air or light. The peroxides thus formed do not have to be registered by the manufacturer or importer of diethyl ether, or by any downstream user or distributor of the substance on its own, in a preparation or in an article.

Finally, the decomposition products from paint, where the decomposition is caused by the activity of mould and the products from the bleaching of coloured textiles, which occurs due to the exposure to sunlight, could also be seen as examples falling under this entry.

2. Substances which result from a chemical reaction that occurs incidental to storage of another substance, preparation or article.

Substances may present a certain level of inherent instability. The reaction products resulting from the inherent decomposition of substances do not need to be registered as it would be impractical; they are generated incidentally and without the awareness of the manufacturer or importer of the original substance.

An example of substances that could be covered by this entry are peroxides that are formed from ethers (e.g. diethyl ether, tetrahydrofuran), not only when these are exposed to light and air (see point 1 above), but also upon storage. These peroxides do not need to be registered. Note however, that the potential risks associated with the presence of peroxides in ethers must be taken into account in the assessment of the ethers. Other examples include partially polymerised drying oils (e.g. linseed oil) and decomposition of ammonium carbonate to form ammonia and carbon dioxide (especially if stored above 30°C).

3. Substances which result from a chemical reaction occurring upon end use of other substances, preparations or articles and which are not themselves manufactured, imported or placed on the market.

The end use of a substance on its own, in a preparation or in articles can result in an intended chemical reaction, such as during the use of an adhesive. However, provided that the reaction products obtained cannot be regarded as having been isolated from a manufacturing process or having been placed on the market, these reaction products are exempted from the registration provisions. Note, however, that the potential risks associated with the substances produced must be taken into account in the assessment of the precursors/reactants of the reaction. Please note

that the term “end use” is not limited to the use of a substance by professional or private consumers but includes any intended downstream use of a substance in the supply chain, provided it is not part of a manufacturing process of a substance.

Examples of substances covered by this entry are the products produced from the use of adhesives and paints, combustion products of petrol during the use of cars, and the reaction products of bleaching agents during washing of textiles.

This entry also covers substances present as ionic mixtures in water-based solutions as a result of mixing salts, acids and bases without creating new covalent bonds. Registration would be inappropriate for these substances as the resulting ion pairs are not manufactured substances as such and isolated from the solution, but formed as part of the chemical equilibrium in the solution only. This applies if all acids, bases and salts mixed (i.e. introduced into the solution) have already been registered by an actor up the supply chain (or are exempted from registration) and the chemical safety assessment covers the use of a certain acid, base or salt in the relevant ionic mixture so as to identify a potential change of the hazardous properties of the mixture compared to its constituents, due to the presence of the salts formed in solution.

The toxicological and ecotoxicological properties of salts are partially dependent on the properties of their acidic and alkaline constituents and must be covered in the respective chemical safety assessment of those constituents, with special attention to SVHC properties. The properties of salts and the corresponding acids and bases can be significantly different. For example, acetic acid is corrosive, whereas sodium acetate is not. Some amines display toxicity that the amine salts do not.

Examples for ionic mixtures can be found with detergent and personal care products, e.g. alkyl benzene sulphonic acids and/or fatty acids will in the presence of sodium hydroxide and/or amines be converted into ionic salts. Another example is metal working fluids where the same can happen between various bases (such as amines) and acids without leading to new covalently bound substances, but an equilibrium mixture of salts is formed.

It must be emphasised that deliberate neutralisation of acids or bases to form the corresponding salts, including neutralisation during formulation, is usually a manufacturing process and is not covered by this entry.

4. Substances which are not themselves manufactured, imported or placed on the market and which result from a chemical reaction that occurs when a substance (in this context the substances are described below) functions as intended.

In some cases the mode of action of a substance performing a specific function involves a chemical reaction. Provided that this reaction does not take place during a deliberate manufacturing process, the substances resulting from this chemical reaction do not need to be registered as the risks of the substances produced will be assessed through the assessment of the precursors of the reaction.

It is important to note:

- The exemption only applies to the substances generated when the substances listed in Annex V(4)(a) and (b) function as intended, but it does not apply to the substances listed in Annex V(4)(a) and (b) themselves. In other words, the registration obligations apply to the manufacture, import or placing on the market of the groups of substances listed in Annex V(4)(a) and (b) and where a chemical safety report is required, it should cover such a use and the risks from the products of the reaction. This rule is only applicable to reactions occurring during the use, but not during the manufacture, of a substance listed in Annex V(4)(a) and (b). For example, a neutralisation reaction for the purpose of manufacturing a substance is not covered by this rule.

- The substances resulting from a chemical reaction that occurs when a substance belonging to one of the groups listed in Annex V(4)(a) or (b) functions as intended are exempted but the substances thus formed are subject to registration whenever they are manufactured, imported or placed on the market in other circumstances.

Subparagraph (a)

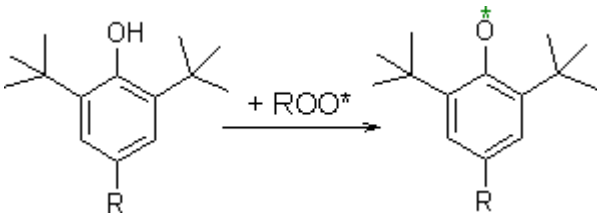
In section (a) of this entry, a comprehensive list of groups of precursors for substances exempted in accordance with this paragraph is provided. This list of precursors includes, inter alia:

i. Antioxidants

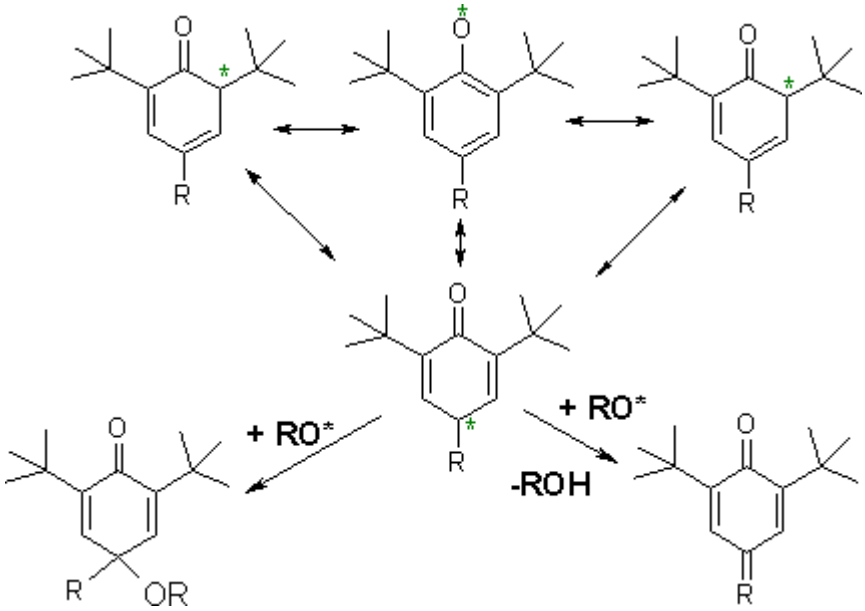
An antioxidant is a substance capable of slowing down or preventing the unwanted modification of other molecules (substances) caused by oxidation. Antioxidants inhibit oxidation reactions by being oxidized themselves. As a result, antioxidants are often reducing agents.

The antioxidant itself, if manufactured or imported, would normally need a registration under REACH. However, the substance(s) arising from the antioxidant while executing its functionality (to remove radical intermediates) does not need to be registered.

Example: Phenols used as antioxidants (e.g. 2,6-bis(tert-butyl)-4-methyl-phenol (EC No: 204-881-4; CAS No: 128-37-0):



The phenoxy radicals generated are very stable due to their ability to build numerous mesomeric forms and are not subject to registration.



The end-products of the oxidation reaction are also not subject to registration.

Another example of this could be the production of the reaction product of the antioxidant tert-Butyl-hydroxyanisol, used to protect fatty acids from oxidation (with oxygen from air).

ii. Corrosion inhibitors

A corrosion inhibitor is a substance that, when added, even in small concentrations, stops or slows down corrosion of metals and alloys. One can distinguish between anodic and cathodic inhibitors depending on which reaction should be inhibited but both types are exempted. Chemical corrosion inhibitors build a protective layer on the metal by a chemical reaction between the metal which has to be protected and the inhibitor. The substances formed during this reaction are not subject to registration; however the metal and the inhibitor normally have to be registered.

iii. Precipitation inhibitors

Precipitation is the process of separating a substance from a solution as a solid. Inhibitors are substances which inhibit or prevent the processes needed for this to take place. Therefore precipitation inhibitors inhibit or prevent the formation of a solid in a solution. While the precipitation inhibitor itself has to be registered, the chemical products resulting from the reaction between the precipitation inhibitor and substances in the solution need no registration.

iv. Chelating agents

The function of chelating agents, also called ligands, chelants, chelators or sequestering agents, is to form a complex ion.

While the manufacture, import and placing on the market of chelating agents is subject to registration, the reaction products from the complexation of an ion with the chelating agent do not need to be registered if these complexes are not themselves manufactured, imported or placed on the market.

It has to be clarified that complexes consisting of chelated ions must be registered if they are themselves manufactured, imported or placed on the market.

Example:

The chelating agent dimethylglyoxime is subject to registration. When this chelating agent is used by an end user to complex nickel ions, the resulting nickeldimethylglyoxime complex does not need to be registered, unless it is manufactured, imported or placed on the market itself (e.g. by a formulator or importer).

v. Coagulants and flocculants

A coagulant is a chemical substance used to contribute to the molecular aggregation of substances present in a solution into particles.

A flocculant is a chemical substance used to promote the aggregation of suspended particles present in a liquid into a macroscopic mass called floc.

Coagulation and flocculation are two techniques commonly combined and are used for instance to remove dissolved organic matter and particles in suspension from water. The substances derived in the coagulation/flocculation process are not subject to registration, unless they are themselves manufactured, imported or placed on the market.

An example of a coagulant used for the coagulation/flocculation process in the purification of water is aluminium sulphate (EINECS no 233-135-0; CAS no 10043-01-3). When aluminium sulphate is added to the water to be treated, a complex series of reactions (including the hydrolysis of aluminium sulphate) takes place that are required for the purpose of coagulation and flocculation.

While the general registration provisions apply to the manufacture or import of aluminium sulphate, the substances derived from aluminium sulphate in the coagulation/flocculation process are not subject to registration. It should be noted that this entry does not specifically mention anti-coagulants, as used e.g. to stabilise blood. These anti-coagulants, should, however, be seen as a stabiliser under this entry.

vi. Surfactants

A surfactant is a surface active agent, i.e. a substance that, because of its design, seeks out the interface between two distinguished phases, thereby altering significantly the physical properties of those interfaces through the modification of some superficial or interfacial activity. The interfaces can independently be liquid, solid or gaseous immiscible liquids, a solid and a liquid.

One example of a surfactant is an **emulsifier**, i.e. a substance that lowers the interfacial tension between immiscible liquids (e.g. oil and water) thereby allowing them to mix.

Whenever a chemical reaction takes place with a substance in the context of its use as surfactant, the substances thus formed do not have to be registered.

For instance, the manufacture or import of a surfactant used for the waterproofing treatment of leather, whereby the surfactant chemically reacts with the surface of the leather, is subject to the registration provisions. The products derived from the surfactant as a result of its reaction with leather are however exempted from the registration provision.

vii. Quality control agents

A quality control agent is a substance used to qualitatively or quantitatively determine a specified parameter in a product for keeping an established quality.

Examples of quality control agents include solutions used for the Karl-Fisher titration techniques. In accordance with these techniques, a series of chemical reactions take place which involve water and the substances constituting the quality control preparations. While the substances in the preparation are subject to registration, the reaction products obtained as a result of the titration are exempted from registration.

viii. Lubricants

A lubricant is a substance applied between two moving surfaces to reduce the friction and wear between them. A lubricant provides a protective thin film which allows two surfaces to be separated while performing a certain functionality by reducing the friction between them.

Some lubricants contain reactive functional groups, with the purpose of creating a boundary layer to the surface(s) to be lubricated. Any substance thus generated is exempted from the registration provisions unless manufactured or placed on the market themselves.

An example of this could be a **lubricant** that reacts with the surface of a metal to provide a physically attached 'oil' layer.

ix. pH Neutralisers

A pH neutraliser is a substance used to adjust the pH-value of a solution, generally an aqueous solution, to the intended level. pH neutralisers are for instance used to balance the pH of drinking water.

The neutralisation mechanism is based on acido-basic reaction between the pH neutraliser and the liquid to be treated. The reaction products from the pH neutraliser are exempted from the registration provisions. This does not apply to the deliberate formation of salts from acids or bases.

While the pH neutraliser, if manufactured or imported, is subject to registration, the reaction products from the pH neutraliser are exempted from the registration provisions.

x. Adhesion promoters

An adhesion promoter is a substance which is applied to a substrate to improve the adhesion of a product to the substrate. The adhesion is created by the formation of strong bonds (including both covalent and non-covalent bonds) between the adhesion promoter and the surfaces of the products to be bound. In addition, some adhesion promoters in a first step chemically react to generate the adhesion properties (e.g. silanes hydrolyse into silanols in contact with moisture) and the substance thus obtained acts as adhesion promoter in a second step.

The substances thus formed during the use of an adhesion promoter are exempted from the registration provisions.

While the adhesion promoter, if manufactured or imported, is subject to registration, the substances formed during the use of an adhesion promoter are exempted from the registration provisions.

xi. Agglomerating agents

An agglomerating agent is a substance that binds solid particles together to form an agglomerate. The agglomeration process can involve chemical reactions between the agglomeration agent and the solid particles to be agglomerated. The substances derived in the agglomeration process are not subject to registration, unless they are themselves manufactured, imported or placed on the market.

xii. De-emulsifiers

A de-emulsifier is a substance used to facilitate the separation of two immiscible liquid phases (or more) present as an emulsion. A general mechanism of action for the de-emulsification is based on the interaction between the de-emulsifier and the emulsifier present in the emulsion, and results in the destabilisation of this emulsion. The interaction between the de-emulsifier and the emulsifier may for instance consist of a chemical reaction between the two substances. In this case, the substances derived in the de-emulsifying process are not subject to registration, unless they are themselves manufactured, imported or placed on the market.

xiii. Fire retardants

A fire retardant is a substance used to protect a combustible material, for instance certain plastics or wood, against fire. The flame retardants mechanism of action generally involves chemical reactions with the flame retardants under the conditions of a fire. While the flame retardant itself is subject to registration, the substances formed during the exposure of the treated material to heat / fire are not.

Subparagraph (b)

In this section, the group of substances exempted from the registration provisions is an extension of the list of substances provided in subparagraph (a). Whenever a substance is used with the aim of providing a specific physicochemical characteristic and where a chemical reaction takes place for the purpose of this application, the substances thus produced do not have to be registered, provided that these substances are not themselves manufactured or placed on the market. The substance produced and its risks shall be assessed through the life-cycle assessment of the precursors/reactants of the reaction.

For instance, the chemical generation of luminescent light from glowing sticks can be the result of the chemical reaction taking place inside the stick between luminol, a base and hydrogen peroxide in the presence of a catalytic amount of copper (II) sulphate. While the registration provisions apply to the manufacture or import of the different substances necessary for the production of chemiluminescence, the substances produced for the generation of luminescence in glowing stick are exempted from registration.

Another example is the use of calcium hydride (CaH_2) as a dewatering agent. The dewatering mechanism is based on the chemical reaction taking place between calcium hydride and water, which results in the formation of calcium hydroxide ($Ca(OH)_2$). While the registration provisions apply to the manufacture or import of calcium hydride, the calcium hydroxide formed as a result of its use as dewatering agent is exempted from registration as such (but should be included in the CSR for calcium hydride).

5. By-products, unless they are imported or placed on the market themselves.

'By-product' means a production residue that is not a waste; a 'production residue' is a material that is not deliberately produced in a production process.[1] EINECS defined by-products as "*substances which are produced without separate commercial intent during the manufacture of another substance*."

A by-product consumed by the same legal entity does not need to be registered while the by-product placed on the market is regarded as a substance that does need to be registered.

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[1] Commission Communication on waste and by-products (COM(2007) 59 final)

6. Hydrates of a substance or hydrated ions, formed by association of a substance with water, provided that the substance has been registered by the manufacturer or importer using this exemption.

Hydrates of a substance are characterised by the fact that water molecules are linked ancillary valently by molecular interactions, in particular by hydrogen bond to other molecules or ions of the substance. Solid hydrates contain water of crystallization in a stoichiometric ratio, an example would be $NiSO_4 \cdot 7\ H_2O$. This formula only expresses that one molecule of $NiSO_4$ can crystallise with seven molecules of water.

For the purposes of this Annex, hydrates and water free forms (anhydrous) of compounds shall be regarded as the same substance. Hydrated and anhydrous forms have different chemical names and different CAS numbers. However, one registration dossier has to be submitted. The water-free form should be registered, and hydrated forms are covered by this registration.

Examples			
Name and formula	**CAS number**	**EC number**	**Rule**
Copper sulphate (Cu . H2O4S)	7758-98-7	231-847-6	
Sulphuric acid copper(2+) salt (1:1), pentahydrate ($Cu.H_2O_4\ S\ .5\ H_2O$)	7758-99-8		This substance is covered by its anhydrous form (EC number: 231-847-6)

Producers of hydrates that only change the hydration state of a substance (i.e. changes the number of water molecules associated with the substance) are downstream users if the anhydrous form is registered up their supply chain. The relevant uses should be covered in any applicable exposure scenario.

It is important to note that a registrant who wants to make use of the exemption under this entry needs to add up the quantities of the anhydrous form and the different hydrated forms in his technical dossier (but excluding the water which is attached to the parent molecule).

Some double salts, e.g. $(Ca(NO_3)_2 + (NH_4NO_3)$ as used in fertilizers, are not considered substances but instead as mixtures. The individual substances present in double salts must be registered. However, other types of double salts are not mixtures e.g. alum which is a hydrated potassium aluminium sulphate $(KAl(SO_4)_2 \cdot 12H_2O)$ used for a range of industrial processes or potassium sodium tartrate $(KNaC_4H_4O_6 \cdot 4H_2O)$ which is used as a food additive. Please note that

double salts of this type which are hydrates, such as alum, are exempted along the lines of this exemption.

7. The following substances which occur in nature, if they are not chemically modified:

Minerals, ores, ore concentrates, raw and processed natural gas, crude oil, coal.

This exemption comprises certain 'substances which occur in nature', if they are not chemically modified, independently from whether or not they are classified as dangerous according to Directive 67/548/EEC.

This group of substances is characterised via the definitions given in Article 3(39) and 3(40):

According to Article 3(39), 'substances which occur in nature' means a naturally occurring substance as such, unprocessed or processed only by manual, mechanical or gravitational means, by dissolution in water, by flotation, by extraction with water, by steam distillation or by heating solely to remove water, or which is extracted from air by any means.

The definition can be split into single parts which help in obtaining a clearer understanding of its whole:

Naturally occurring substances[2] as such: means, substances obtained, for example, from plants, micro-organisms, animals (e.g. blood, milk), or certain inorganic matter such as minerals, ores and ore concentrates, crude oil, coal, natural gas. In this context, it should be noted that whole living or dead organisms (e.g.

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[2] Naturally occurring substances that fulfil this definition share a single EINECS entry :

EINECS No 310-127-6 CAS No : 999999-99-4

Substance Name: Naturally occurring substances

Description: Living or dead material occurring in nature as such which is chemically unprocessed, or which is extracted from air by any means or physically processed only by manual, mechanical or gravitational means, by dissolution in water, by flotation or by heating solely to remove water.

yeast, freeze-dried bacteria) or parts thereof (e.g. body parts, branches, leaves, flowers etc.) are not considered as substances, preparations or articles in the sense of REACH. The latter would also be the case if these have undergone digestion or decomposition resulting in waste as defined in Directive 2006/12/EC, such as manure or anaerobic digestion product of biowaste, even if, under certain circumstances, these might be seen as non-waste recovered materials[3].

Unprocessed: no treatment at all of the substance takes place.

Processed only by manual, mechanical or gravitational means: parts of the substance as such may for instance be removed by hand or by machine (e.g. by centrifugation). If minerals are processed *only* by mechanical methods, e.g. by grinding, sieving, centrifugation, flotation, etc., they are still considered to be the same naturally occurring minerals as originally mined.[4]

By dissolution in water: the only solvent which can be used is water. The dissolution by any other solvent or mixture of solvents or mixture of water with other solvents disqualifies the substance as naturally occurring.

By flotation: separation without chemical reaction.

By extraction with water: cut-off process (e.g. fractionating, concentration) for separating certain constituent or constituents from a mixture of constituents by using water only.

By steam distillation: distillation of naturally occurring substances with water vapour as carrier for the separation of certain constituent(s) without chemical reaction.

Heating solely to remove water: purification or concentration of a substance by removing water by heat while no chemical reaction occurs.

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[3] This explanation is without prejudice to discussions and decisions to be taken under Community waste legislation on the status, nature, characteristics and potential definition of such materials, and may need to be updated in the future.

[4] (ECHA, 2007) Guidance for identification and naming of substances under REACH p.38

Extracted from air by any means: substances which occur naturally in air, extracted by applying any methods and solvents as far as no chemical reaction occurs.

According to Article 3(40), a '**not chemically modified** substance' means: a substance whose chemical structure remains unchanged, even if it has undergone a chemical process or treatment, or a physical mineralogical transformation, for instance to remove impurities.

Whenever one of the constituents of the final isolated substance which occurs in nature undergoes a chemical reaction during its processing, the substance must be regarded as having been chemically modified.

The specific substances covered by the exemption are:

i. Minerals

A mineral is defined as a combination of inorganic constituents as found in the earth's crust, with a characteristic set of chemical compositions, crystalline forms (from highly crystalline to amorphous) and physical properties. In general minerals are inorganic and most of them are crystalline. Whenever minerals are manufactured in accordance with any method other than the ones mentioned in the definition of 'substances which occur in nature' these substances are not exempted from the obligation to register.

Minerals which occur in nature are covered by the exemption if they are not chemically modified. This applies to naturally occurring minerals, which have undergone a chemical process or treatment, or a physical mineralogical transformation, for instance to remove impurities, provided that none of the constituents of the final isolated substance has been chemically modified'. Synthetic minerals are not covered by this exemption.

ii. Ores

Ores is a general expression for mineral aggregates or rocks from which metals or metal components can be extracted as well as for mineral aggregates whose mining have an economical benefit.

The ores themselves can be regarded as substances which occur in nature and which therefore are exempted from the obligation to register. It should be noted however, that when ores are processed or treated with methods not mentioned in the definition of 'substances which occur in nature', or with methods which modify the chemical structure of the final substance, the final 'product' of the treatment can

normally not be regarded as a substance which occurs in nature and hence will need to be registered.

Example: The iron ore type 'banded ironstone formation (BFI)' which is composed predominantly of magnetite ($Fe^{2+}Fe_2^{3+}O_4$) and quartz is processed mechanically in the first steps by means of coarse crushing and screening, followed by rough crushing and fine grinding to comminute the ore to the point where the crystallised magnetite and quartz are fine enough that the quartz is left behind when the resultant powder is passed under a magnetic separator. Up to this stage all substances, including the original ore, created through the whole process are regarded as substances which occur in nature.

To convert magnetite to metallic iron it must be smelted or sent through a direct reduction process. Magnetite (or any other iron ore) must be powdered and mixed with coke. During the process in the blast furnace the following reduction or oxidation-reactions take place:

Air blast and coke: $2C + O_2 \rightarrow 2CO$

Carbon monoxide (CO) is the principal reduction agent

Stage One: $3Fe_2O_3 + CO \rightarrow 2Fe_3O_4 + CO_2$

Stage Two: $Fe_3O_4 + CO \rightarrow 3FeO + CO_2$

Stage Three: $FeO + CO \rightarrow Fe + CO_2$

During this manufacturing process different treatments take place which disqualify the final iron as a substance occurring in nature:

- Heating was not solely applied for removing water
- The iron oxide is subject to a reduction / oxidation reaction which is a chemical reaction leading to a new / different substance from the starting material

As a consequence, iron is regarded as a substance for which the registration obligations need to be fulfilled.

iii. Ore concentrates

Ore concentrates are extracted from the original ore mostly by mechanical measures or flotation resulting in mineral-rich fraction which is used for further

processing of e.g. metals. Such processes include, but may not be limited to, sorting; magnetic separation; electrostatic separation; preferential crushing, grinding and milling; sieving and screening; hydrocycloning; filtration and flotation.

Therefore ore concentrates are generally regarded as substances which occur in nature provided the manufacturing processes are only mechanical and/or by flotation, (e.g. grinding, sieving, centrifugation, etc.), or other processes that remove impurities but leave the chemical structure of the final isolated constituents of the substance which occurs in nature unchanged (e.g., leaching or washing out of impurities).

iv. Natural gas

Natural gas is a gaseous fossil fuel which consists predominantly of saturated hydrocarbons. Natural gas can have different compositions depending on the source and can be divided into three groups:

- natural gas from pure natural gas deposits is composed of methane and small amounts of ethane; it is saturated with water vapour and contains liquid and free water.

- natural gas from coal deposits is composed of methane, small amounts of ethane and variable amounts of nitrogen and carbon dioxide; it is saturated with water vapour and contains liquid and free water.

- natural gas from crude oil deposits contains in addition larger amounts of ethane, propane, isobutene, hexane, heptane, carbon dioxide, hydrosulfides, helium, nitrogen and arsenic compounds.

- natural gas from condensate and distillate deposits which contains besides methane and ethane also higher amounts of hydrocarbons with more than 7 C-atoms.

The raw natural gas itself, without further processing, can be regarded as a substance which occurs in nature. However, raw natural gas has to be processed to make it suitable for the use by residential, commercial and industrial consumers. The processed natural gas is almost pure methane and is very much different from the raw natural gas.

The main processing of raw natural gas for removing by-products can be summarised as follows:

- removal of liquid water and natural gas condensate
- removal of acid gases (hydrogen sulphide, carbon dioxide) by e.g. amine treatment or polymeric membranes
- removal of water vapour by e.g. absorption or by using membranes
- removal of nitrogen and / or helium by e.g. cryogenic process or absorption process
- removal of natural gas liquids by e.g. cryogenic low temperature distillation process
- separation into ethane, propane, butanes (iso-butane, n-butane) and hydrocarbons with C +5 carbon atoms by a fractionation train
- final natural gas which is almost pure methane

It has to be emphasised that only methane which is processed from raw natural gas can be regarded as natural gas. Methane processed from other sources than fossil, e.g. biogas, is not regarded as natural gas.

The European INventory of Existing commercial Chemical Substances (EINECS) lists one entry for natural gas which gives the following description:

EINECS number: 232-343-9 CAS number: 8006-14-2

Natural gas

Raw natural gas, as found in nature, or a gaseous combination of hydrocarbons having carbon numbers predominantly in the range of C1 through C4 separated from raw natural gas by the removal of natural gas condensate, natural gas liquid, and natural gas condensate/natural gas.

Natural gas isolated through any further processing of the raw natural gas, other than the steps listed in the definition of a substance occurring in the nature, can in fact not be regarded as a substance which occurs in nature.

v. Crude oil

Crude oil is a lipophilic mixture of hydrocarbons which is incorporated into the earth's crust. Crude oil can consist of more than 17,000 constituents and is one of the most complex mixtures of organic compounds. The formation of crude oil is

based on sapropel of flat inshore waters emanated from carbohydrates, proteins and fats from small animals and small plants under the influence of bacteria, enzymes, pressure, mineral catalyst etc. The crude oil production is based on mechanical measures which qualifies crude oil as a substance which occurs in nature.

However, when processing and separating crude oil, the constituents or mixtures of constituents arising from these processes can normally no longer be regarded as substances which occur in nature, for example:

EC number: 272-871-7 CAS number: 68918-99-0

Gases (petroleum), crude oil fractionation off

A complex combination of hydrocarbons produced by the fractionation of crude oil. It consists of saturated aliphatic hydrocarbons having carbon numbers predominantly in the range of C1 through C5.

vi. Coal

Coal is a solid fossil fuel formed by carbonisation of plants. There are two types of coal; brown coal and black coal which differ in their carbon content. Brown coal contains 60 – 80 % carbon and black coal contains 80 – 98 % carbon. Coal is usually processed only by mechanical means which qualifies coal as a substance which occurs in nature.

8. Substances which occur in nature other than those listed under paragraph 7, if they are not chemically modified, unless they meet the criteria for classification as dangerous according to Directive 67/548/EEC or unless they are persistent, bioaccumulative and toxic or very persistent and very bioaccumulative in accordance with the criteria set out in Annex XIII or unless they were identified in accordance with Article 59(1) at least two years previously as substances giving rise to an equivalent level of concern as set out in Article 57(f).

This exemption comprises 'substances which occur in nature' not set out in paragraph 7, unless they are classified as dangerous according to Directive 67/548/EEC. The essential elements to be considered are:

- Substances must meet the definition of a 'substance which occurs in nature' as defined in Article 3(39)[5].

- Substances are not exempted if they are classified as dangerous according to Directive 67/548/EEC. This means that a substance is not exempted if it is either on Annex I of Directive 67/548/EEC or the manufacturer or importer of the substance has assessed it as meeting the criteria set out in Annex VI of Directive 67/548/EEC. In addition, substances meeting the criteria for PBTs and vPvBs in Annex XIII are also not exempted nor are substances giving rise to an equivalent level of concern according to Article 59(f) and were included on the candidate list (according to Article 59(1) at least two years previously[6].

It should be emphasised that an absence of information on the properties of a substance does not equate to the absence of hazardous properties. Many substances that might fall into the 'substances which occur in nature' category have insufficient information available on them to conclude that they are not dangerous. To exempt such substances would undermine the aims of REACH to gather information on substances in order to determine their potential hazards.

9. The following substances obtained from natural sources, if they are not chemically modified, unless they meet the criteria for classification as dangerous according to Directive 67/548/EEC with the exception of those only classified as flammable [R10], as a skin irritant [R38] or as an eye irritant [R36] or unless they are persistent, bioaccumulative and toxic or very persistent and very bioaccumulative in accordance with the criteria set out in Annex XIII or unless they were identified in accordance with Article 59(1) at least two years previously as substances giving rise to an equivalent level of concern as set out in Article 57(f):

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5 See point 7 above for guidance on this definition.

6 In the latter case if a substance occurring in nature is identified according to Article 57(f) and included in the candidate list it no longer is subject to an exemption under this point from a date two years after the date of its inclusion and should be registered on that date.

Vegetable fats, vegetable oils, vegetable waxes; animal fats, animal oils, animal waxes; fatty acids from C6 to C24 and their potassium, sodium, calcium and magnesium salts; glycerol.

This exemption comprises substances obtained from natural sources if they are not chemically modified, unless they meet the criteria for classification as dangerous according to Directive 67/548/EEC, with the exception of those only classified as flammable [R10], as a skin irritant [R38] or as an eye irritant [R36] or a combination thereof. Substances meeting the criteria for PBTs and vPvBs are also not exempted nor are substances giving rise to an equivalent level of concern according to Article 59(f) and were included on the candidate list (according to Article 59(1) at least two years previously[4].

This exemption is not limited to naturally occurring substances in the sense of the definition of Article 3(39). This means that substances falling under this exemption can be obtained through other processes than those described in Article 3(39), including a chemical modification (e.g. ester hydrolysis to obtain fatty acids). 'Obtained from natural sources' means that the original source must be a natural material (e.g. plants or animals). In this context, 'not chemically modified' means that the substance covered by this exemption is not further chemically modified (e.g. a fatty acid is only covered as the substance itself and not in any chemically modified form except their potassium, sodium, calcium and magnesium salts, which are explicitly mentioned in Annex V.9)

The groups of substances that are covered by this exemption are:

- Vegetable fats, vegetable oils and vegetable waxes. Vegetable fats and oils are substances derived from plants that are composed of triglycerides. Nominally, oils are liquid at room temperature and fats are solid. A wax is composed of non-glycerolic esters of long chain fatty acids esterified with long chain fatty alcohols, triterpenic alcohols and sterols. An example for a vegetable wax is carnauba wax.

  In general, vegetable oils originate from the seeds of oilseed plants, although some other parts of plants may also yield oils. This exemption exclusively applies to vegetable fats, vegetable oils and vegetable waxes but does not cover essential oils. Essential oils are hydrophobic liquids of complex composition, derived from plants, containing volatile organic compounds, such as alcohols, aldehydes, ketones, phenols, esters, ethers and terpenes, in varying proportions.

- Animal fats, animal oils, animal waxes. These are normally rendered tissue fats that can be obtained from a variety of animals. Nominally, oils are liquid at room temperature and fats are solid. A wax is composed of non-glycerolic esters of long chain fatty acids esterified with long chain fatty alcohols, triterpenic alcohols and sterols. Examples of edible animal fats are lard (pig fat), fish oil and butter. Examples of animal waxes are bee wax and lanolin.

- Fatty acids are carboxylic acids often with a long unbranched aliphatic tail (chain) which is either saturated or unsaturated. The entry in Annex V exempts fatty acids with chains containing between 6 to 24 carbons, and their potassium, sodium, calcium and magnesium salts.

  Fatty acids covered by this exemption are only partly available in free form in natural sources like fats and oils but must be obtained from them through ester hydrolysis of the parent glyceride (i.e. the fat or oil).

- Glycerol (EC No: 200-289-5, CAS No: 56-81-5) is also commonly called glycerine or propane-1,2,3-triol and forms the backbone of triglycerides bound to a number of fatty acids.

10. The following substances if they are not chemically modified:

Liquefied petroleum gas, natural gas condensate, process gases and components thereof, coke, cement clinker, magnesia.

This exemption comprises a number of substances that are exempted unless they are chemically modified[7]:

i. Liquefied petroleum gas (LPG)

In general, liquefied petroleum gas comprises the hydrocarbons propane, propene, butane, butene and mixtures thereof which are extracted as by-products during the distillation and cracking of crude oil in oil refineries as well as during the processing of raw natural gas. These gases and their mixtures can be liquefied

[7] See points 7 and 8 above for guidance on this definition

easily by applying a relatively low pressure. For example, commercially supplied butane and propane mixtures would fall under this category.

EINECS is listing LPG with the following entry:

EC number: 270-704-2 CAS number: 68476-85-7

Petroleum gases, liquefied

A complex combination of hydrocarbons produced by the distillation of crude oil. It consists of hydrocarbons having carbon numbers predominantly in the range of C3 through C7 and boiling in the range of approximately -40°C to 80°C (-40°F to 176°F).

ii. Natural gas condensate

Natural gas condensate is a low-density mixture of hydrocarbon liquids that are present as gaseous components in the raw natural gas. It condenses out of the raw natural gas if the temperature is reduced below the hydrocarbon dew point temperature of the raw natural gas. Natural gas condensate is regarded as a by-product of the processing of the natural gas. Depending on the processes used to isolate it, natural gas condensate may be regarded as a substance which occurs in nature.

EINECS number 272-896-3 CAS number 68919-39-1

Natural gas condensates

A complex combination of hydrocarbons separated and/or condensed from natural gas during transportation and collected at the wellhead and/or from the production, gathering, transmission, and distribution pipelines in deeps, scrubbers, etc. It consists predominantly of hydrocarbons having carbon numbers predominantly in the range of C2 through C8.

iii. Process gases and components thereof

Process gases are not naturally occurring substances. The expression ‘process gas’ can be regarded as an umbrella term for all kinds of gases produced during certain technical processes. Any risks from the process gas should be covered in the Chemical Safety Assessment of the substances involved in the process itself.

An example of a ‘process gas’ is blast furnace gas. This gas is produced during the combustion of coke in blast furnaces in the iron and steel industry. It is recovered

and used as a fuel partly within the plant and partly in other steel industry processes or in power stations equipped to burn it.

Other examples of process gases include: welding fumes, wood dust, soldering fumes, etc.

iv. Cement clinker

Cement clinker is a component of cement. Cement is regarded as a preparation composed of cement clinker, gypsum and other constituents depending on the cement type. Cement clinker is manufactured from the raw materials limestone, clay, bauxite, iron ore and quartz, grounded to a fine powder which is heated under oxidising conditions up to around 1400°-1450° C, at which temperature partial melting (sintering) takes place, resulting in drab granules. This process warrants that chemical bonds in the raw material cease to exist and new bonds are irregularly formed through material melting, producing the granules containing mainly tricalcium silicate, dicalcium silicate, dicalcium aluminate ferrite, tricalcium aluminate and calcium oxide. The melted material is rapidly cooled (quenched) to preserve its reactive mineral constituents.

Cement clinker does not have an EINECS number but it is very close in composition to "Cement, portland, chemicals" and/or "Cement, alumina, chemicals". Both of these substances have entries in EINECS (included below for reference):

1. EINECS number 266-043-4 CAS number 65997-15-1

Cement, portland, chemicals

Portland cement is a mixture of chemical substances produced by burning or sintering at high temperatures (greater than 1200°C (2192°F)) raw materials which are predominantly calcium carbonate, aluminium oxide, silica, and iron oxide. The chemical substances which are manufactured are confined in a crystalline mass. This category includes all of the chemical substances specified below when they are intentionally manufactured in the production of Portland cement. The primary members of the category are Ca_2SiO_4 and Ca_3SiO_5. Other compounds listed below may also be included in combination with these primary substances

$CaAl_2O_4$	$Ca_2Al_2SiO_7$
$CaAl_4O_7$	$Ca_4Al_6SO_{16}$
$CaAl_{12}O_{19}$	$Ca_{12}Al_{14}Cl_2O_{32}$

$Ca_3Al_2O_6$ $Ca_{12}Al_{14}F_2O_{32}$

$Ca_{12}Al_{14}O_{33}$ $Ca_4Al_2Fe_2O_{10}$

CaO $Ca_6Al_4Fe_2O_{15}$

$Ca_2Fe_2O_5$

2. EINECS number: 266-045-5 CAS number: 65997-16-2

Cement, alumina, chemicals

High-Alumina cement is a mixture of chemical substances produced by burning or sintering at high temperature (greater than 1200°C (2192°F)) raw materials which are predominantly calcium carbonate, aluminium oxide, silica, and iron oxide. The chemical substances which are manufactured are confined in a crystalline mass. This category includes all of the chemical substances specified below when they are intentionally manufactured in the production of high-alumina cement. The primary members of this category are $CaAl_2O_4$, $Ca_4Al_2Fe_2O_{10}$, $Ca_{12}Al_{14}O_{33}$, and Ca_2SiO_4. Other compounds listed below may also be included in the combination with these primary substances.

$CaAl_4O_7$ $Ca_2Al_2SiO_7$

$CaAl_{12}O_{19}$ $Ca_4Al_6SO_{16}$

$Ca_3Al_2O_6$ $Ca_{12}Al_{14}Cl_2O_{32}$

CaO $Ca_{12}Al_{14}F_2O_{32}$

Ca_3SiO_5 $Ca_6Al_4Fe_2O_{15}$

$Ca_2Fe_2O_5$

v. Magnesia

Magnesia is a natural form of magnesium oxide found as a mineral also called periclase.

There is no information currently available that magnesia meets the criteria for classification as dangerous according to Directive 67/548/EEC.

vi. Coke

Coke is a black, combustible residue of the coking of coal, predominantly consisting of carbon. The coking of coal is a refining procedure of coal which applies a heat treatment on coal under exclusion of air. The produced quantities of coke, coal gas, tar and by-products are depending on the modification, quality and quantity of coal and the applied temperature range. Coke can also be formed from petroleum.

EINECS number 266-010-4 *CAS number 65996-77-2*

Coke (coal)

The cellular carbonaceous mass resulting from the high temperature (greater than 700°C (1292°F)) destructive distillation of coal. Composed primarily of carbon. May contain varying amounts of sulfur and ash.

EINECS number 265-080-3 CAS number 64741-79-3

Coke (petroleum)

A solid material resulting from high temperature treatment of petroleum fractions. It consists of carbonaceous material and contains some hydrocarbons having a high carbon-to-hydrogen ratio.

11. The following substances unless they meet the criteria for classification as dangerous according to Directive 67/548/EEC and provided that they do not contain constituents meeting the criteria as dangerous in accordance with Directive 67/548/EEC present in concentrations above the lowest of the applicable concentration limits set out in Directive 1999/45/EC or concentration limit set out in Annex I to Directive 67/548/EEC, unless conclusive scientific experimental data show that these constituents are not available throughout the life-cycle of the substance and those data have been ascertained to be adequate and reliable:

Glass, ceramic frits.

According to the scientific literature glass is the state of a substance rather than a substance as such. For legislative purposes, it can best be defined through its starting materials and production process, similar to many other UVCB substances. EINECS has several entries for glasses as follows:

Glass, nonoxide, chemicals (EC: 295-731-7), Glass, oxide, calcium magnesium potassium sodium phosphosilicate (EC: 305-415-3), Glass, oxide, calcium magnesium sodium phosphosilicate (EC: 305-416-9) and Glass, oxide, chemicals (EC: 266-046-0)[8];

A frit is a ground glass or glaze used in pottery; some materials have to be fritted before they can be used because they are soluble or toxic.

EINECS lists frits under the following entry:

Frits, chemicals (EC: 266-047-6).

The glass and frits substances are very similar in composition and manufacturing process.

Only those types of glass and ceramic frits are exempted which do not have any significant hazard properties:

- Firstly, glass or ceramic frits are only to be exempted if they (as substances as such) do not meet the criteria for classification as dangerous according to Directive 67/548/EEC. There are two possibilities to assess this criterion: look at the glass itself or look at the starting materials.

- Secondly, they are not exempted if the substance contains constituents meeting the criteria as dangerous in accordance with Directive 67/548/EEC that are present in concentrations above the lowest of the applicable concentration limits set out in Directive 1999/45/EC or concentration limit set out in Annex I to Directive 67/548/EEC, unless conclusive scientific experimental data show that these constituents are not available throughout the life-cycle of the substance and those data have been ascertained to be adequate and reliable. In this case, industry has to look at the constituents after the production of the glass (constituents could be different than the starting materials) to see if they are classified and present above the relevant concentration limit. If this is the

[8] Please note that the description following the heading in the EINECS listing of these substances is part of the substance entry and in most cases it is most decisive for substance identification.

case then they are not exempted unless the constituent is not available throughout the life-cycle of the substance[9].

It is the responsibility of manufacturers or importers to assess and document the conclusive scientific data to demonstrate their substance(s) fulfil these criteria.

Man Made Vitreous Fibres (mmvf) included in Annex I to Directive 67/548/EEC are not covered by this exemption as they meet the criteria in Annex VI of that Directive. In addition, mmvf, which are not listed in Annex I to Directive 67/548/EEC, but that meet the criteria for classification as dangerous according to Annex VI of Directive 67/548/EEC are also not to be exempted.

12. Compost and biogas

This exemption covers compost when it is potentially subject to registration, i.e. when it is no longer a waste, and is understood as being applicable to substances consisting of solid particulate material that has been sanitised and stabilised through the action of micro-organisms and that result from the composting of any biowaste capable of undergoing aerobic decomposition in its entirety.

This explanation is without prejudice to discussions and decisions to be taken under Community waste legislation on the status, nature, characteristics and potential definition of compost, and may need to be updated in the future.

Biogas is gas produced by the biological breakdown of organic matter in the absence of oxygen and consists of mainly methane.

13. Hydrogen and oxygen

This exemption covers two substances, hydrogen (EC Number 215-605-7) and oxygen (EC Number 231-956-9).

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[9] ECHA will be asked to expand on the guidance related to this point to take into account the guidance produced in RIP 3.6 that is relevant to this point.