Questions & Answers for cyclic siloxanes D4, D5 and D6

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What are silicones?

“Silicone” is a generic term referring to a class of synthetic polymers that are based on a framework of alternating silicon and oxygen (siloxane) bonds with at least one organic group attached to the silicon atom via a direct carbon-silicon bond. They have an inorganic silicon-oxygen (Si-O) backbone and are defined as inorganic or hybrid substances.

https://globalsilicones.org/explore-silicones/what-are-silicones/

https://www.silicones.eu/science/production/chemistry-polymerisation/

Silicones are used in hundreds of applications where their special performance is needed. They are used as adhesives, they are used in the manufacture of insulation materials, they impart unique sensory benefits, and they have excellent mechanical/optical/thermal resistance among many other properties. They are used, for example, in medical technologies, renewable energy and energy saving solutions, cosmetic and cleaning products, as well as digital technologies, construction and transportation.

What are D4, D5 and D6 and where are they used?

Octamethylcyclotetrasiloxane (D4), Decamethylcyclopentasiloxane (D5) and Dodecamethylcyclohexasiloxane (D6) are used to create a diverse range of silicone materials that provide unique, beneficial characteristics to a wide variety of applications and products across sectors, including construction, electronics, engineering, health care, cosmetics and personal care. These are essential raw materials for tailoring polysiloxane backbones resulting in high performing additives for the coating and inks industry.

D4, D5 and D6 are most frequently used as chemical intermediates, meaning that the substances are employed in the manufacturing process but only present as low-level impurities in the end products.

What does SVHC mean?

SVHC stands for “Substance of Very High Concern”.

Who made the SVHC decision?

The decision to identify D4, D5, D6 as SVHCs was made by the ECHA Member States Committee (MSC), which is composed of experts nominated by EU Member States and ECHA.

The MSC members were asked to review the technical dossiers submitted by Germany for D4 and D5, and by ECHA for D6, as well as the comments received during the public consultation. The mandate of these experts is to assess and confirm the scientific basis underpinning the SVHC proposals, and not to assess the potential impact.

Why were D4, D5 and D6 listed as SVHC?

Based on the criteria used in REACH, D4 meets the criteria for Persistent, Bioaccumulative and Toxic (PBT) substances, and D5 and D6 meet the criteria for very Persistent, very Bioaccumulative (vPvB) substances.

In addition, D5 and D6 are considered PBT when they contain more than 0.1% D4.

This led to a nomination by EU Member States to the list of SVHCs. However we believe that the REACH criteria do not allow the full range of relevant scientific evidence to be considered and that not all relevant scientific evidence was thoroughly taken into account prior to decision making.

What does it mean in practice that D4, D5 and D6 are listed as SVHC?

An SVHC listing is not a ban on the use of silicone polymers. Nor is it a ban or a restriction on the use of D4, D5 and D6 'as such'. Silicone polymers can be used safely in all products.

Formal identification of PBT/vPvB properties entails communication and risk management measure obligations. The complexity of this information varies according to the actors in the supply chain:

- Silicone manufacturers will need to implement on site, and recommend to downstream users, risk management measures which minimize exposure and emissions, throughout the lifecycle of the substance that results from the manufacture or identified use.
- The relevant safety data sheets will be updated by individual companies without undue delay, as applicable (substances and mixtures, when the substance is individually present at levels $\geq$ 0.1%).
- Suppliers of articles (final articles as placed on the market after processing and treatment, including those that are partly based on silicone) containing D4, D5 or D6 in a concentration above 0.1% (weight by weight), either intentionally added as an ingredient or present as an impurity, will need to provide sufficient information to their customers (industry, professional users, distributors) to allow safe use of the article. This information must contain as a minimum the name of the substance.
- Consumers can request similar information and have the right to receive an answer within 45 days of the receipt of the request.
- Producers or importers of articles have to notify ECHA if their article contains D4, D5 or D6 totalling over one tonne per producer or importer per year and in a concentration above 0.1% (weight by weight, per substance). The notifications must be submitted no later than 6 months after the inclusion on the candidate list. No notification is required if exposure of humans and the environment to the substance can be excluded during the use and disposal of the article.

The notification needs to include the following information:

- the identity and contact details of the company
- the identity of the substance and its registration number, if available
- the tonnage range of the substance in the notified article(s)

- a brief description of the use(s) of the substance in the article(s) and of the uses of the article(s)

The following website explains the obligations resulting from inclusion of SVHCs in the Candidate List:

https://echa.europa.eu/candidate-list-obligations

The following website explains the notification process for substances in articles:

https://echa.europa.eu/support/dossier-submission-tools/reach-it/notifying-substances-in-articles

On what basis did the EU make its PBT/vPvB determinations for D4, D5 and D6?

The EU made its determinations based on the REACH PBT/vPvB criteria.

The REACH criteria to assess bioaccumulation were intended only to be used for organic (carbon-based) substances, not inorganic substances. D4, D5 and D6 have an inorganic part in the molecule.

Therefore, the criteria used to assess whether D4, D5 and D6 are bioaccumulative do not reflect the unique chemistry of siloxanes. As a matter of fact, recent scientific studies have concluded that these legal criteria are not appropriate for estimating the behaviour of siloxanes in the environment.

The criteria for bioaccumulation assessment focus on one factor only, namely bioconcentration.

As a result, the bioconcentration factor data was weighted stronger than the non-bioconcentration data – for example, the trophic magnification data (data measuring the average relative increase (decrease) in concentration of a substance over an entire food chain). By not applying a robust scientific weight-of-evidence determination, weighing all available data and taking the unique properties of siloxanes into account, the scientific assessment of D4, D5 and D6 was effectively skewed.

Experts from the Member States Committee considered the field data to be inconclusive for the time being. However, real-world monitoring data show that D4, D5 and D6 do not bioaccumulate in the environment. These data are important, as monitoring data provide evidence of actual levels of a given substance in the environment. Real-world data allow scientists to assess actual exposure levels, and these data can be used to refine and better calibrate predictive models that may otherwise not be appropriate to be used for silicone materials.

In the case of D4, D5 and D6, the methodology based on bioconcentration factors may significantly overestimate bioaccumulation, but there is also a risk of underestimating bioaccumulation in the case of other substances. Accurate PBT/vPvB assessment based on the latest science should be the prevailing policy driver.

What restrictions exist for D4, D5 and D6?

In January 2018, a restriction on the use of D4 and D5 was published in the EU Official Journal (Regulation (EC) No. 2018/35). The scope of the restriction is limited to wash-off cosmetic products with a D4 or D5 concentration equal to or greater than 0.1% by weight of either substance. This restriction aims at emissions to water, which was identified as a potentially critical compartment, and is effective since end of January 2020. The industry has accepted the restriction as a proportionate measure, is committed to support it and monitor the effect in the environment.

In April 2017, the European Chemicals Agency (ECHA) published a restriction intention addressing D4 and D5 in leave-on personal care products and other consumer/professional products (e.g. dry cleaning, waxes and polishes, washing and cleaning products) in concentrations greater than 0.1 %. D6 was later added to this intention. The restriction dossier was published in January 2019. After the public consultation on Annex XV report the SEAC draft opinion was published on 5 December 2019.

It concluded that the restriction proposed on D4, D5 and D6 is the most appropriate EU wide measure to address the identified risks, as concluded by RAC. On 16 March 2020, ECHA announced that SEAC has adopted its final opinion supporting ECHA's proposal to restrict the placing on the market of D4, D5 and D6 as substances, as constituents of other substances, or in mixtures in a concentration equal to or greater than 0.1 % weight by weight of each substance.

The restriction process on the "use of D4, D5 and D6 in leave-on cosmetic products and other consumer or professional products" – those not covered by the previous "wash-off" restriction – as well as the addition of D6 to the "wash-off" restriction, are expected to be adopted in 2023.

What exemptions exist from the restrictions?

The restriction proposal as defined by RAC and SEAC has latest been modified in March 2020. Besides the restriction proposal it contains several exemptions by way of derogation, among these:

- Industrial use as a monomer in the production of silicone polymer
- Industrial use as an intermediate in the production of other organosilicon substances
- Industrial use as a monomer in emulsion polymerization
- Industrial use in formulation and/or (re-) packing of mixtures
- Industrial production of articles
- Industrial use in non-metal surface treatment
- Industrial use as laboratory reagent in Research & Development activities

In addition, by way of derogation, the restriction shall not apply to the placing on the market of mixtures that contain silicone polymers with residues of:

a) D4 or D5 or D6 in a concentration equal to or less than 1% w/w, for use in adhesion, sealing, gluing and casting
b) D5 in a concentration equal to or less than 0.3% w/w or D6 in a concentration equal to or less than 1% w/w, for use as medical devices (as defined in Directive 93/42/EEC or in the Regulation (EU) 2017/745) for dental impression.
c) D4 in a concentration equal to or less than 0.5% w/w, or D5 or D6 in a concentration equal to or less than 0.3 % w/w for use as protective coatings (including marine coatings).
d) D5 in a concentration equal to or less than 1% w/w or D6 in a concentration equal to or less than 3% w/w, for (i) rapid prototyping and mould making, and (ii) high performance uses stabilised by quartz filler.
e) D4 or D5 or D6 in a concentration equal to or less than 0.2% w/w, for use as (substance based) medical devices as defined in Directive 93/42/EEC or in the classification rule 21 set in Annex VIII to the Regulation (EU) 2017/745.
f) D4 or D5 or D6 in a concentration equal to or less than 0.5 % w/w, for use as adhesion promoters.
g) D6 in a concentration equal to or less than 1 % w/w, for professional use in the cleaning or restoration of art and antiques.
h) D5 or D6 in a concentration equal to or less than 1 % w/w, for use in pad printing, or manufacturing of printing pads.
i) D4, or D5, or D6 in a concentration equal to or less than 1 % w/w, for use in 3D-printing.

What does the authorisation of D4, D5 and D6 mean for silicone polymers?

On 14 April 2021, ECHA announced its recommendation to add D4, D5 and D6 to REACH Annex XIV to the authorisation list (Annex XIV). This recommendation follows D4, D5 and D6 inclusion in the REACH Candidate List in 2018 and is part of standard REACH procedure.

According to the background documents for authorisation intention the volumes of imported polymers have not been considered for priority assessment. It is also recognized, that siloxane cyclics are used as precursors for polymers and can remain as impurities with concentrations >0.1% in the silicone polymer. Use of such polymers would also not require authorisation. **Thus it can be concluded that D4, D5 and D6 as impurities of polymers are out of scope of the intended authorisation recommendations by ECHA**

Are D4, D5 and D6 POPs (Persistant Organic Pollutants)?

ECHA, the European Chemicals Agency, has launched on 15 June 2023 a public consultation on a draft scientific dossier to assess whether D4, D5 and D6 meet the scientific criteria to be listed under the Annex B[1] of the Stockholm Convention's Persistent Organic Pollutants (POP). The consultation is open for comments until 10 August 2023. This is not a decision that D4, D5 and D6 meet the POP criteria nor that they should be listed under the Convention at this stage.

Currently, scientific discussions are ongoing as to whether these substances meet the criteria of the Convention, such as the long-range transport potential (LRT) and back-deposition to remote locations. In collaboration with authorities and other stakeholders, the industry is organising a comprehensive field study in the Antarctic region to assess whether D4, D5 and D6 can be transported and accumulate in remote environments. We expect initial results to be available in Q3 2024. In addition, a second study is being conducted with the Norwegian Air Institute (NILU) in the Arctic, with first results expected in Q4 2023.

What does it mean in practice if D4, D5 and D6 will be added to ANNEX B of Stockholm Convention?

This question could not be answered in detail at this time. But there are several risks related to the proposal of listing these substances.

The EU Commission confirmed that their intention is to propose a listing under the Stockholm Convention to stop direct uses of D4, D5, D6 in consumer applications globally, whilst protecting polymer production, transportation and availability via a broad acceptable purpose for use of these substances as transported intermediates for polymer production. For context, direct (non-intermediate) use of these substances accounts for less than 2% of usage globally, whilst >98% is used for polymer production (intermediate use). Hence, such a broad acceptable purpose would apply to >98% of the uses of these substances. No acceptable purpose that would allow for broad intermediate use, accounting for most of the volumes of a given substance, has ever been granted under the Stockholm Convention.

A final recommendation to obtain a broad acceptable purpose for transported intermediates will ultimately be taken by the Stockholm Convention's Persistent Organic Pollutants Review Committee (POPRC). Past and current practice at the POPRC show that stakeholder negotiations drive exemptions to a very granular level, regardless of the initial proposal intentions. The POPRC will need to submit its recommendation to the involved parties (COP) for a final decision. The COP can follow fully, partly, or disregard that recommendation. It is very difficult (even for the EU) to predict the final outcome of a proposal as the listing is overall the result of political bargaining between parties.

The Commission indicated that on-site intermediate use of D4, D5, D6 would be automatically exempted as closed-system site-limited intermediates (CSSLI). However, the Stockholm Convention does not define CSSLI conditions, whose definition is left instead to individual Parties. The standard applied in Europe is 'Strictly Controlled Conditions' (SCC). In the EU, SCC are defined in Article 18(4) (a) to

[1] Annex B of the Stockholm Convention lists the specific chemicals that are considered POPs and subject to restrictions and control measures.

(f) of the REACH Regulation. To our knowledge, no other Party has set specific requirements for how CSSLI should be implemented within their jurisdictions.
In a Stockholm listing scenario, such stringent measures would need to be applied at D4, D5, D6 manufacturing sites but also at the downstream user sites who use these substances to make silicone polymers. The cost of implementing such robust emission containment measures would likely drive many players out of the market.

A POP listing would negatively impact the production and use of silicone polymers also because D4, D5, D6 residues in polymers will be restricted or prohibited. The Stockholm Convention generally exempts POPs occurring as "unintentional trace contaminants" (UTCs) in products and articles from the requirements under Annexes A and B. However, there is no precise definition of UTCs. This means that Parties must implement their own definitions and thresholds for UTC exemptions to enable an effective implementation of the Convention. While the EU Commission could set a UTC limit value at 0.1% in the EU, to mirror the concentration limits set under REACH (with which industry is working towards complying and will comply to it latest by the entry into force of the REACH restriction), it is not guaranteed that other Parties will not set more stringent limits. This would create distortions in the market for silicone polymers, which would be subject to different rules across different countries.

Would a POP listing have an impact on the recycling of silicone waste?

A POP listing of D4, D5, D6 would trigger automatic constraints/bans impacting the ability to ship, recycle, and safely mange waste. For instance, the Stockholm Convention and the Basel Convention on the Control of Transboundary Movements of Hazardous Wastes and their Disposal have a joint mandate on POPs waste and have agreed to cooperate closely on establishing levels of destruction and irreversible transformation necessary to ensure that POPs characteristics do not persist. EU POPs Regulation (Regulation 2019/1021) envisages that POPs can only be recovered from the waste for the sole propose to be destroyed. Recycling silicones will only work technically and economically at large economies of scale, with transport of the waste streams secured globally and across Europe. With a listing of D4, D5, D6 under the Stockholm Convention and, subsequently in the Basel Convention, this transport would be only workable when: a) residuals are set to at least 0.1% by weight in the Basel Convention, and b) under a Stockholm Convention listing, exemptions are included to produce D4, D5, D6 through recycling processes. These two conditions are essential and yet extremely difficult to secure in a highly uncertain negotiation of both treaties, which the EU Commission would trigger with a POP listing of D4/5/6.

"Allowed" concentrations of POP content in waste – so-called low-persistent-organic-pollutant content (LPC) – are set in the General Technical Guidelines on the environmentally sound management of wastes. If COM were unable to secure workable LPC values, all waste containing silicone polymers from D4, D5, D6 would go to incineration. The industry would not be able to recycle devices with silicone parts, volatile materials containing D4/5/6, and silicone polymers with residues below 0.1% w/w of D4/5/6.

There is a clear risk that a POP listing of D4, D5, D6 will hamper and impede recycling.

Have other countries considered real-world data as part of their assessment?

In both countries Canada and Australia, governmental authorities have evaluated the impact of D4, D5 and D6 on the environment, and in each instance, regulators relied on all available science and risk-based evaluations that consider weight-of-evidence. As a result, both countries decided not to impose any restrictions on the use of these substances in commerce. The U.S. is also considering an evaluation of D4 and has worked collaboratively with industry to produce exposure data that the US EPA (Environmental Protection Agency) requested for its assessment.

What are the socio-economic consequences of an SVHC decision?

Identifying D4, D5 and D6 as SVHCs is damaging to investments, innovation and competitiveness, as it causes considerable uncertainty for customers on a global level.

Silicone polymers rely on D4, D5 and D6 as building blocks (monomers) for their manufacturing. Silicone materials are widely used and difficult to substitute because of their durable, safe and highly effective mechanical, optical and thermal properties. Critical applications include construction, transportation, lighting, alternative energy, cosmetic, cleaning, electronics and medical uses.

It is important to note that SVHC candidate Listing of D4, D5 and D6 does not constitute a ban on manufacturing or use of silicones, or on the use of D4, D5 and D6 ‘as such’.

Are there alternatives to silicones, with similar properties?

Siloxanes are a group of substances characterized by a chain of alternating silicon (Si) and oxygen (O) atoms. Because siloxanes have an inorganic backbone, they are different from organic (carbon-based) substances. The structure and functionality of these chemical compounds drive the specific combination of properties of siloxanes including: high propensity to repel water, low water solubility and volatility.

Siloxanes are a key element in the production of silicones. Silicone materials offer a host of useful characteristics including: Thermal stability (high and low temperature), resistance to oxidation, ozone, UV exposure, good wetting, spreading, and flow, low electrical conductivity, and water repellency (among many others). While alternative materials may provide one or a few of these properties, there are no alternative materials which could provide the same combination of unique properties.

In addition, using silicones, siloxanes and silane products generates greenhouse-gas emission reductions that outweigh the impacts of production and end-of-life disposal by a factor of 9. In other words, for every ton of CO2 emitted, the use of silicones allows for savings 9 times greater. This is at the top of the range of previous estimates made for chemistry applications across the board.

Silicones can continue to be used as SVHC identification of D4, D5 and D6 does not constitute a ban or a restriction on silicone polymers, or on the use of D4, D5 and D6 ‘as such’.

Can silicones be used safely?

Yes, silicones can be used safely in all products. Silicones remain safe, when used as intended. Silicones are not new on the market.

In fact, they have been used for more than six decades. If they were indeed very persistent and bioaccumulative, we would expect to see very high and increasing levels in the environment since their uses significantly grew over time – however, observed levels monitored in a wide variety of temperatures and surroundings are extremely low (close to the detection limit).

The many years of use have therefore not led to any environmental concern and based on the observed data we do not expect this to change. Multiple lines of evidence show the environmental levels are not increasing.

The PBT criteria under REACH rely predominantly on laboratory-based testing and do not consider these real-life data.

However, in order to comply with the officially recognized PBT designation, the silicones industry has committed to minimize emissions at all levels. A first step is the development of an emissions management guide to support our value chain in managing emissions.

In addition, going beyond regulatory obligations, the silicones industry is currently in the process of establishing a voluntary product stewardship program to this effect.

Monitoring results show that concentrations of D4 and D5 in wastewater are already typically below the predicted baseline, and in the case of D4, already consistent with predicted post-restriction levels.

What does that mean for the Evonik products?

For the vast majority of Evonik's products D4 and D5 are only used as reactive substances, e.g. for the production of polymers. We have already optimized over the past years our production processes to minimize the residual content of D4 and D5 in our products.

Many of Evonik's products are being used as additives in single digit percentage concentrations in our customers formulations. And most of our products contain already less than 0.1 % of each of the cyclic siloxanes. We clearly expect that we can continue to serve these applications, as the socio-economic benefit clearly outweighs the potential reduction of emissions. We will provide such socio-economic arguments to the authorities.

Evonik in line with the Silicone Industry is assessing future scenarios. Although Industry works intensively with legislative bodies to avoid unnecessary and disproportionate rules, Evonik cannot exclude the restrictions for direct use of cyclic siloxanes and for the content of cyclic siloxanes in consumer and professional products. Evonik believes that this may oblige us to further reduce the content of cyclic siloxanes in products for consumer and professional use, e.g. for household care products. This might be required in about 3 years from now. We will closely work with our customers to determine the best path forward with our products in the various applications.

What is the position of Evonik?

Evonik is a member of Silicones Europe and GSC-Global Silicones Council and supports the position that the ongoing regulatory activities are disproportionate and not warranted for protection of the environment. Industry bases their conclusion on the unique properties and behaviour of cyclic siloxanes. The silicones industry is committed to responsible stewardship and is determined to address environmental risks through developing and supporting independent science and monitoring studies, which inform and guide measures. The industry will continue to work closely with regulatory authorities and with downstream users around the globe to ensure that silicones can continue to provide all the benefits and innovations for which they are used with confidence. Due to the specifics of silicone chemistry it is not possible to produce silicone polymers and silicone copolymers under industrial conditions with 'zero D4 / D5'. During polymerization a certain amount of cyclic siloxanes will remain unreacted and can only be reduced afterwards to certain levels, which depend on the polymers and work-up conditions.

In general, we confirm that Evonik is fully committed to Silicone technology and is working hard to define jointly with authorities a reasonable path forward, which allows to continue to use Silicone products and their special properties.

Where can I find further information?

ECHA Restrictions

- Wash-off Personal Care products: https://echa.europa.eu/substances-restricted-under-reach/-/dislist/details/0b0236e182463cd3
- Leave-on Personal Care and other consumer and professional products: https://echa.europa.eu/registry-of-restriction-intentions/-/dislist/details/0b0236e181a55ade
- ECHA Annex XV report: https://echa.europa.eu/documents/10162/039f5415-d7a2-b279-d270-0d07e18f6392

SVHC

- RMOA: https://echa.europa.eu/rmoa
- SVHC candidate list https://echa.europa.eu/candidate-list-table
- SVHC legal obligations https://echa.europa.eu/candidate-list-obligations

Authorisation

- Background document for octamethylcyclotetrasiloxane (D4): https://echa.europa.eu/documents/10162/7cc92a5f-ca14-f23b-ac4d-fdd8c6471ab5
- Background document for decamethylcyclopentasiloxane (D5): https://echa.europa.eu/documents/10162/58d230eb-6cbc-f2c1-3bed-2ddf408329c2
- Background document for dodecamethylcyclohexasiloxane (D6): https://echa.europa.eu/documents/10162/da907b89-f29d-6e65-db94-8e9777addacd

Silicones Europe & Global Silicones Council

- SVHC statement:
  https://www.silicones.eu/the-addition-of-d4-d5-and-d6-to-the-candidate-list-under-reach-is-disproportionate-and-endangers-critical-beneficial-uses/
  https://globalsilicones.org/regulation/eu/substances-of-very-high-concern/
- Properties and behaviour of cyclic siloxanes in the environment
  https://www.silicones.eu/science/environment/
  https://globalsilicones.org/safety/environment/
- Monitoring study
  https://www.silicones.eu/wp-content/uploads/2023/02/silicone-research_an-industry-commitment.pdf
- Toolbox for minimising environmental emissions
  https://www.silicones.eu/wp-content/uploads/2023/02/Cyclosiloxanes_Toolbox_Version-Nov-2019.pdf