FINAL REPORT

MUDP forprojekt

[August/2021- April/2022]

PFAS-free friction reducing additive for use in lubricants

March 31, 2022

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Miljøteknologisk Udviklings- og Demonstrationsprogram

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FINAL REPORT

PFAS-free friction reducing additive for use in lubricants

FACTS ABOUT THE PROJECT

Project period: 1st of August 2021 to 1st of April 2022
Project participants: CeramicSpeed A/S
Grant from MUDP: Budget DKK 610.448,52 of which DKK 427.314 in grants.
Project manager: Lina Søbjerg Madsen

SAMMENDRAG

I dette forprojekt har CeramicSpeed undersøgt muligheden for at substituere PTFE med et mere miljøvenligt alternativ til brug i CeramicSpeeds SLT smøremiddel til kuglelejer. Teknologisk Institut har hjulpet med at udarbejde en liste over mulige substitutions-kandidater. Fra denne liste har CeramicSpeed udvalgt 8 kandidater, som herefter er blevet testet individuelt som substitut i CeramicSpeeds SLT-formulering. Alle 8 kandidater tilfører enten sammenlignelig eller øget friktionsreducerende egenskaber til SLT-formulering som ved brug af PTFE. 3 af kandidaterne giver endda en øget friktionsreducerende egenskab samtidig med, at de ikke påvirker performance af SLT smøremidlet negativt under brug.

AIM OF THE PROJECT

The aim of the project is to investigate the possibility of finding an environmentally friendly substitution of PFAS in high-performance lubricants used in CeramicSpeed's production of high-quality bearings. In the project, environmentally friendly, PTFE alternatives must be identified, and the performance of lubricant test formulations with PTFE alternatives must be evaluated and undergoing friction, performance, and endurance test to ensure the quality of the lubricant.

RELEVANCE OF THE PROJECT

In the food industry, the use of PFAS, in the form of PTFE, is frequently used as a friction-reducing additive or lubricant in the food industry. This is in particular due to the fact that PTFE is an approved Food Contact Material (FCM), and currently, there are no alternative friction reducing FCM which is comparable to PTFE in terms of performance. Unfortunately, PFAS has a negative impact on the environment in particular the aquatic environment. The inappropriate environmental consequences of PFAS substances have resulted in initiatives from the Danish Environmental Protection Agency and others EU countries which propose a strong restriction on the use of PFAS. Although PTFE in itself is not considered to be directly harmful to health, it will, for example, when disposed of and incinerated, be converted to toxic organic fluorine compounds, such as trifluoroacetate TFA, which are persistent

and toxic to aquatic organisms. Furthermore, PTFE also acts as a microplastic in watercourses and gardens. Both currently and in the future large sources of PFAS emissions in the environment are predicted due to production, use and disposal of PTFE in the industry.
In the field of lubricants, a phasing out of PFASs will be conditional of the possibility of substituting with a high-performance alternative that reduces friction while at the same time do not negatively affect performance of the lubricant. CeramicSpeed supplies bearings for food production, but also bearings, bicycle chains and lubricants for cyclists. In both segments, it will be of health and environmental benefit if PFAS-free alternatives were developed as these lubricants come in close contact with users, service personnel, food and ultimately washes / wears off and ends up in nature.

MAIN RESULTS

CeramicSpeed has tested 8 different additives to determine if these have friction reducing properties in CeramicSpeed's SLT ball bearing lubricant. The 8 selected candidates are Boron nitride, graphene, graphite, silver nanoparticles, SiO_2 nanoparticles, SiO_2-silan nanoparticles, PEEK, and ZnO nanoparticles. CeramicSpeed's SLT ball bearing lubricant consists of an oil-plastic matrix which slowly dispenses oil to the ball bearing while preventing water, dirt and particles from penetrating the ball bearing. CeramicSpeed's SLT lubricant extends the bearing life significantly compared to greases when run in harsh environments. The plastic matrix without a friction-reducing additive has very high friction when mounted in a ball bearing, and it is therefore necessary to add a friction-reducing additive. By substituting PTFE with one of the 8 candidates, it was possible to produce a molded plastic matrix for all individual candidates. However, the quality of the plastic matrix was very dependent on the specific additive. Using boron nitride, graphene, graphite or ZnO nanoparticles resulted in a plastic matrix with similar qualities as the plastic matrix with PTFE. Adding silver nanoparticles to the plastic matrix resulted in a very soft matrix, which is unsuitable to be used in a ball bearing hence this will negatively affect the bearing performance and the bearing lifetime. Adding either SiO_2 nanoparticles, SiO_2-silan nanoparticles or PEEK to the plastic matrix resulted in a perforated plastic matrix wherein air holes were distributed throughout the plastic matrix (as a Swiss cheese). Such a perforated plastic matrix is not desirable hence this may result in water, dirt and/or particles to easily penetrate the plastic matrix. The friction was also measured for each of the SLT-additive equipped bearings. The main results from this study showed that none of the additives affected the friction of the SLT bearings negatively i.e., none of them increased the friction in the bearing. Also, SLT bearings with additives of ZnO nanoparticles and silver nanoparticles were measured to have the equal range of friction as SLT bearings with PTFE. Quite surprisingly using the additives; boron nitride, graphene, graphite, SiO_2 nanoparticles, SiO_2-Silan nanoparticles or PEEK in the SLT matrix resulted in bearings with lower friction compared to SLT with PTFE. Based on the initial friction performance, 4 candidates (Boron nitride, SiO_2 nanoparticles, SiO_2-silan, and PEEK) were selected to try and further optimize the SLT-additive formulation in order to decrease friction even further. By optimizing the ratio of the plastic polymers to additive it was possible to obtain up to 30% lower friction, using one of these four additives, compared to SLT with PTFE. Based on these optimization results, we have tested if these candidates affect the performance and oil retention of the SLT-additive bearings. Boron nitride negatively affected the oil reten-

tion and performance of the SLT bearings, and it is therefore not a suitable PTFE substitution candidate in this process. Interestingly, SiO_2 nanoparticles, SiO_2-silan nanoparticles, and PEEK only slightly negatively affected the oil retention. Using these additives, it was possible to optimize the SLT-additive formulation, so the additive did not affect the oil retention and performance of the SLT-additive ball bearings.
As mentioned previously, using SiO_2 nanoparticles, SiO_2-silan nanoparticles, or PEEK in the plastic matrix resulted in a perforated plastic matrix. It was further investigated, if it was possible to produce a molded non-perforated SLT plastic matrix using one of these three additives. By optimizing the production setup, we were in fact able to produce molded non-perforated SLT plastic matrix in this study.

LESSONS LEARNED DURING THIS PROJECT

The Danish Technological Institute has helped identify possible additives that can be used as friction-reducing additives instead of PTFE in CeramicSpeed's SLT lubricant production. The Danish Technological Institute has compiled a list of 18 possible candidates, in which CeramicSpeed has selected 8 candidates (Boron nitride, graphene, graphite, silver nanoparticles, SiO_2 nanoparticles, SiO_2-silan nanoparticles, PEEK and ZnO nanoparticles). The criteria for selecting these additives are: Approved for food contact material (FCM), temperature stability, commercially availability, and environmental considerations. The list of identified and selected additives is given in Appendix A. The Danish Technological Institute has also prepared an environmental assessment of 5 selected PTFE substitutes to determine if the substitutes are better alternatives to the use of PTFE based on environmental impact. The environmental assessment report, in Appendix B, assesses that the additives: Boron nitride, graphite, PEEK and SiO_2 nanoparticles do not pose any greater risk to health and the environment than the use of PTFE, and they can therefore be used as additives. However, silver nanoparticles pose a greater risk to the environment than PTFE and are therefore classified as a regrettable substitute.
We chose initially to test the additives by making a 1:1 substitution of additive with PTFE. This was done to determine if any of the selected additives have friction reducing properties when encapsulated and molded into a plastic matrix. By substituting the list of additives 1: 1 with PTFE, we were also able to detect if the additive negatively affects the molded plastic, but also to determine if the additive has friction-reducing properties when molded in the plastic matrix. The molded plastic matrix is essential, as it is the plastic matrix that protects the ball bearing in harsh environments, but it is also the plastic matrix that dispenses the right amount of oil to the ball bearing (oil retention). If the oil retention is too high, then the oil will leak too quickly from the ball bearing, which reduces the bearing lifetime. Conversely, if the retention is too low, then the oil will remain in the plastic matrix, thereby reducing the amount of oil available for keeping the bearing lubricated, which will also reduce the bearing lifetime.
For all the tested additives, it was possible to produce an SLT plastic matrix. We have also tested each bearing in our bearing-watt-measuring test machine. This test machine was built inhouse and it measures the friction of the bearing under a constant radial load. One challenge of this project was to find the optimum amount of additive in the SLT formulation, which results in an optimum oil retention in the plastic matrix, while at the same time generate the lowest possible friction. This challenge has been solved via a systematic trial-and-error method, wherein the amount of additive has been varied

in the SLT formulation. The respective SLT formulations were then molded into ball bearings and studied by determine the state of the molded plastic, friction, performance, and oil retention in the bearing. We have also developed an in-house test protocol wherein we can determine the oil retention in the bearing, while also measuring friction in the bearing.
Another challenge has been to solve the problem that some additives cause an undesired perforated plastic matrix during the plastic molding and curing process. We have systematically tried to solve the challenge of finding a method to achieve a non-perforated plastic matrix. In order to solve this problem, we became aware that the additives purity, and storage of the additives were of prime importance in order to acquire a suitable plastic matrix.

CONCLUSION AND PERSPECTIVE

The goal of the project was to achieve a SLT lubricant with the same or lower friction-reducing properties as when using PTFE as friction modifier without compromising the performance of the lubricant. It was possible to identify alternative additives to PTFE that both have friction reducing properties while at the same time have a better environmental profile than PTFE. The Danish Technological Institute has identified 18 potential candidates (Appendix A) to obtain low friction in our plastic molded SLT lubricant. Out of this listing, CeramicSpeed selected 8 candidates: Boron nitride, graphene, graphite, silver nanoparticles, SiO_2 nanoparticles, SiO_2-silan nanoparticles, PEEK, and ZnO nanoparticles to test in our SLT formulation. Using inhouse testing facilities, we were able to measure, for each bearing, its friction, performance, and oil retention. We found that it was possible to substitute PTFE with one of 4 candidates (Boron nitride, SiO_2 nanoparticles, SiO_2-silan, and PEEK) to obtain lower friction in our SLT bearings than by using PTFE based SLT. These four candidates all have a better environmental profile than PTFE and it is therefore better to use one of these low-friction additives than using PTFE. It was also possible to optimize the SLT formulation with the three additives (SiO_2 nanoparticles, SiO_2-silan, and PEEK) to obtain a PTFE free-SLT product that does not negatively affect performance of the bearings compared to PTFE-SLT lubricated bearings. We also succeeded in optimizing our production method and setup to accommodate using one of these additives in our future SLT production to eliminate the use of PTFE.
In a preliminary study, we wanted to determine if it was possible to lower friction of a standard grease by adding one of the identified additives that had given successful results in the SLT formulation. We chose the 3 additives (boron nitride, PEEK, and SiO_2 nanoparticles) and added them individually to a ball bearing industrial standard grease. We found that addition of PEEK or boron nitride did not affect, neither positive nor negative, friction in the bearing. However, we found that it was possible to obtain up to 18 percent friction reduction in the bearing by adding an optimized amount of SiO_2 nanoparticles to the grease. In another preliminary study, we wanted to determine if it was possible to lower friction of a standard gear-box oil. We added either PEEK or SiO_2 nanoparticles to the gear-box oil. Quite surprisingly, we found that addition of PEEK or SiO_2 nanoparticles did not have a positive impact on bearing friction, but increased friction in the bearing instead. In these two preliminary studies, we conclude that the 4 identified friction reducing additives that reduce friction in the SLT formulation, do not have universal friction reducing properties in other lubricants such as greases and oils. Generally, the ability

of a lubricant to reduce friction is dependent on the bearings operational rotational speed and temperature. However, in this study we found that the ability of the identified additives to reduce friction is not only affected by the operational properties of the bearing but is also very dependent on the type of lubricant and its composition. Although SiO_2 nanoparticles shows great friction reducing properties and generally do not have an environmental negative impact, we as a company would not want to add SiO_2 nanoparticles to our lubricants. The main reason for this is that SiO_2 nanoparticles are considered harmful if inhaled. Also, inhalation of silica may induce silicosis which may lead to lung cancer in the person handling the silica particles. Even though CeramicSpeed's production facilities could establish precautionary measures to safe handling the use of SiO_2 nanoparticles, we as a company do not want to expose our colleagues to an unnecessary risk.

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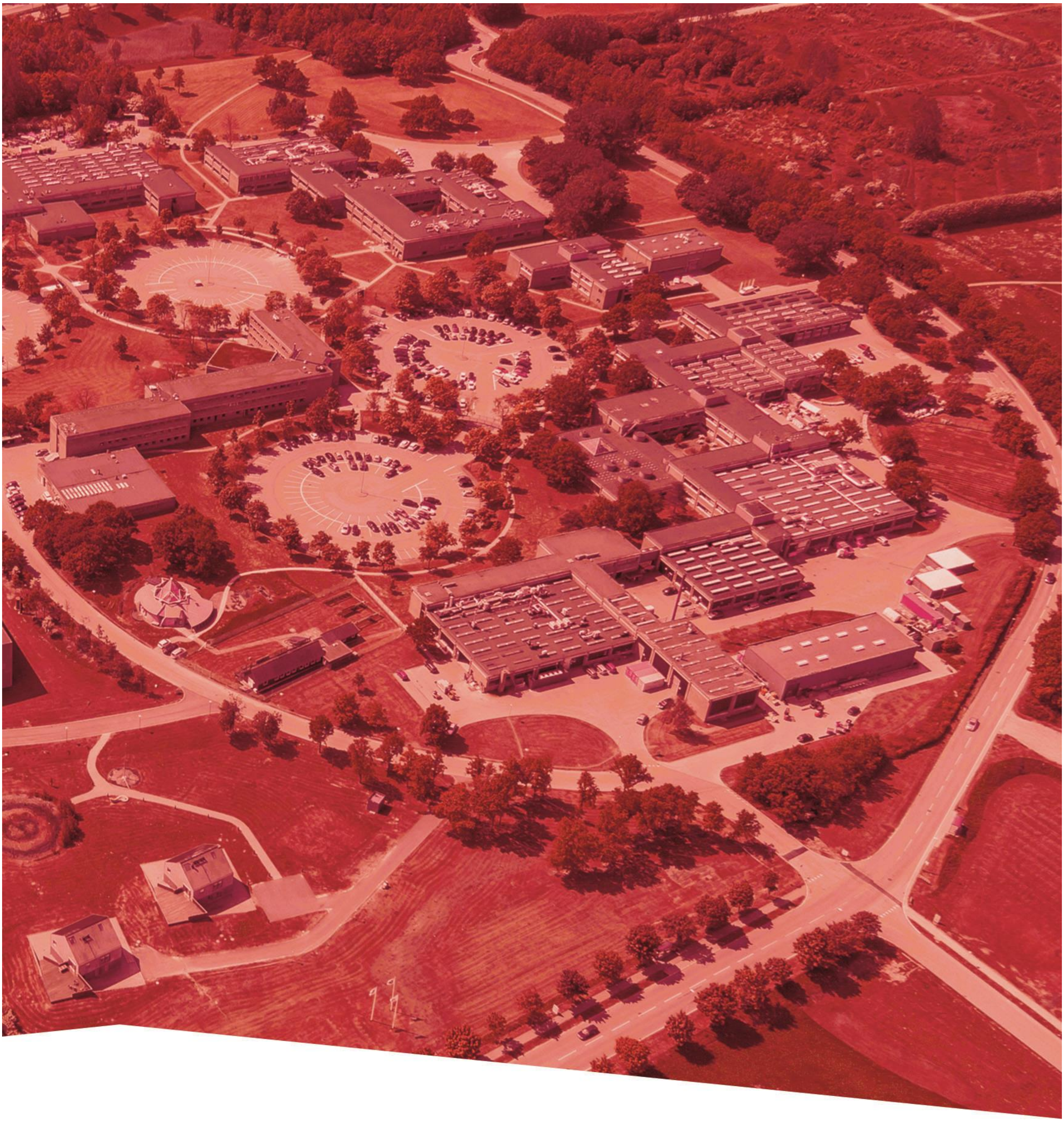
Appendix A: List of identified PTFE substitutes

Selected	Technology	Short Description
Polymer based technologies potential direct substitution of PTFE		
X	PEEK particles (Polyetheretherketone)	FCM, temperature stability, chemical resistant
	PPS particles (PolyphenylenSulfide)	FCM, temperature stability, chemical resistant
	POM particles (Polyoxymethylene)	FCM, temperature stability, chemical resistant
	Nylon-6 filled with oil	(FCM), uncertain how oil and nylon interact
	Polypropylene (PP)	FCM, higher melting point than PE, but below < 150 °C
	Paraffin wax particles	FCM uncertain
Non-polymer based technologies		
	2D inorganic materials	High stability, low friction in 2D, not FCM
X	Nanoparticles (for example. SiO_2, $CaCO_3$, ZrO_2, graphite)	Friction reducing properties in plastic. Not necessarily FCM.
X	Graphene nanoparticles	Expensive material, 2D material with low friction, not FCM.
X	Boron nitride	Already use as friction reducing material in lubricants. Possible to obtain FCM grade.
	AlMgB14	Newly developed inorganic material with low friction. Not FCM.
	Self-lubricating metal-organic framework (MOF)	Microporous structure with lubricant that slowly releases over time.
	Shear-thinning oil (with particles or polymers in the oil)	Oil with lower viscosity at the vicinity of the balls when the ball bearing is in motion.
	Fatty acid amides in PE	Low friction film on PE plastic
	Fullerene-like nanoparticles	Spherical nanoparticles. Non-commercial. Not FCM
	Diamond like carbon particles	
	Silicone oil	Used in low friction applications
	Sol-Gel coated particles	Sol-Gel coatings can be manufactured with low friction however it is uncertain if it is possible to produce sol-gel nanoparticles. Not FCM

Appendix B – The environmental assessment report “PTFE substitution: Environmental and health assessment of alternatives”



PTFE substitution: Environmental and health assessment of alternatives

DANISH TECHNOLOGICAL INSTITUTE

DANISH
TECHNOLOGICAL
INSTITUTE

PTFE substitution: Environmental and health assessment of alternatives

Report in relation to MUDP pre-project partly funded by The Danish Environmental Protection Agency

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February 2022

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Contents

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1. Assignment

As part of a pre-project partly funded by the Danish Environmental Protection Agency, under the MUDP-program, CeramicSpeed A/S (CS) has tasked the Danish Technological Institute (DTI) with evaluating the environmental and health impact of five different materials that are being considered as potential substitutes for Polytetrafluorethylene (PTFE) in CS's Solid Lubrication Technology (SLT) bearings. The materials evaluated in this report are powdered forms of:

- Boron nitride (BN)
- Graphite
- Silver (Ag) nanoparticles
- SiO_2 nanoparticles
- Polyether ether ketone (PEEK)
- Polytetrafluorethylene (PTFE), for reference

2. Conclusion

Based on the investigated listings and safety data sheets of the relevant materials, this environmental and health assessment concludes that both boron nitride, graphite, PEEK and SiO_2 could be used as substitutes for PTFE, as they do not exhibit a higher environmental risk than PTFE for the specific use. Ag nanoparticles exhibit higher risk than PTFE and is hence considered a regrettable substitution for PTFE. It should be noted that SiO_2 nanoparticles are considered harmful if inhaled and use of this material would require establishment of additional precautionary measures in the production facilities at CS. However, this risk is not considered relevant in the final product where the particles will be bound in a plastic matrix.

Ag nanoparticles are listed in both the coRAP and the TEDX list, and current legislative processes may introduce additional harmonized hazard classifications in the future. Currently Ag nanoparticles are classified as very toxic to aquatic life with long lasting effects.

From the available listing and the safety data sheet (SDS) of PTFE alone, there is no environmental argument for substituting PTFE in the current product, however this substitution is motivated by the initiative suggesting a broad European ban on non-essential use of per- and polyfluoroalkyl substances (PFAS).

3. Background

The purpose of the pre-project under MUDP has been to explore the possibilities of replacing the small amount of PTFE in CS's SLT bearings with an environmentally friendly component containing no fluoro-alkyl species. The motivation of this substitution is the initiative from authorities in Germany and the Netherlands, supported by Denmark, Sweden, and Norway, to propose a broad ban on several non-essential uses of PFAS in products. At the time of writing the legislative proposal is being prepared, and it is currently not clear which PFAS species would be included in the proposed ban. The proposal is expected to be submitted by July 15th, 2022. Any restrictions resulting from this proposal are expected to enter into force by 2025.

At the time of writing there are no restrictions from the European Chemical Agency (ECHA) on the use of PTFE in lubricants.

4. Health and environmental assessment methodology

The health and environmental impacts of each candidate material is compared to that of PTFE by two different approaches:

- Listing of substances
- Harmonized hazard classification of product SDS

The listing strategy consists of carrying out a check, for each individual material, of whether the substance is included in any of a number of official lists regarding hazards or suspected hazards related to the included materials. If a material appears in any of these lists, it reflects concern or confirmation of unwanted properties of a given material. In this study the six selected materials' presence on the following six official European or Danish lists was investigated:

- The Candidate List
- Substances restricted under REACH
- SIN-list (Substitute It Now-list)
- CoRAP list (Community Rolling Action Plan list)
- TEDX-list
- The Danish Environmental Protection Agency guide to self-classification

In the case where a material is listed on any of the above, a thorough description on the cause of the listing follows.

The second part of the evaluation for each material is based on harmonized hazard classification of product SDS. The Globally Harmonized System of Classification and Labelling of Chemicals (GHS) is a United Nations system to identify hazardous chemicals and to inform users about these hazards. Any potential hazards stated in the SDS is considered.

The risk of a given hazard is evaluated as the product of two parameters: the severity and the probability. The severity reflects evaluation of the severity of the harmonized hazard classification and the probability reflects evaluation of how probable it is that the user of the SLT is exposed to the hazard, given the amount of material in the SLT and the fact that the material would be bound in a plastic matrix.

For this evaluation all six materials are treated on an equal footing. That is, each of the materials is assumed to be present in the same amount if incorporated into the SLT and is assumed to be bound in a plastic matrix.

Based on listings and classifications of the six materials, it is assessed whether substituting PTFE for the given material in CS's SLT bearings would be considered a regrettable substitution. A regrettable substitution is when a harmful component is replaced by another equally or more harmful component in the attempt to remove harmful components from a product.

4.1. Assessment lists

Six different lists have been used for the listing assessment. Each list has its own specific focus, applications and in some cases legal implications. In the following a short description of each list is given.

4.1.1. The ECHA Candidate List

The Candidate List is the list of substances of very high concern (SVHC) for European authorities. This list is published by ECHA. Suppliers and importers of substances on the candidate list are obligated to implement special measures, e.g. provide a safety data sheet on the substance, communicate on safe use and notify the ECHA if the company produces or imports a product containing more than a total of 1 ton of the SVHC per year, or if the substance is present in their product at a concentration above 0.1 % (w/w). Substances on the candidate list can later in the process be included in the authorization list under REACH.

The purpose of this gradual authorization process (from candidate list to authorization list) is to ensure gradual replacement of harmful substances with less harmful substances or technologies where such technologies are technically and economically available. Substances may be considered SVHC if they possess one or more of the following properties:

- The substance is considered carcinogenic, mutagenic, or toxic for reproduction.
- The substance is persistent, bio-accumulative, and toxic (PBT) or very persistent and very bio-accumulative (vPvB).
- The substance causes an equivalent level of concern as the two points above by any other means.

4.1.2. Substances restricted under REACH

Substances restricted under REACH are specified in the list of Annex XVII to REACH. Annex XVII (also called the restriction list) is published by ECHA and contains all the restrictions of REACH and previous legislation. The list contains all substances and mixtures which are restricted under REACH, including a description of restriction conditions. The restrictions may cover limitations or ban of specific, or all uses of a given substance in Europe.

4.1.3. SIN-list (Substitute It Now-list)

The SIN-list is a list of hazardous chemicals used in a range of different products and manufacturing processes. When a chemical is on the SIN-list, this indicates that the chemical should be removed as quickly as possible, since it poses a threat to human health and the environment. The SIN-list is developed by the non-profit organization ChemSec, who collaborates with scientists and technical experts within environmental, health and consumer organizations. The list is based on trustworthy, publicly available information from existing databases and scientific studies.

4.1.4. CoRAP list (Community Rolling Action Plan list)

The CoRAP list contains substances that one of the EU member states has either evaluated or plans to evaluate. The motivation for the evaluation is the suspicion that a substance may possess a harmful effect.

The list contains the member state evaluating/planning to evaluate the substance, the year of the (planned) evaluation and a short description on the concern of the substance. Furthermore, the list provides access to detailed information on the reason for the initial concern motivating the inclusion of the substance on the CoRAP list (the justification document) as well as the evaluation report on the findings on the evaluation (in case evaluation is completed). Substances included in the CoRAP list have not necessarily been evaluated yet and thus the raised concern is indicative and not exhaustive or conclusive. The list therefore indicates substances which may be considered harmful and could be subject to legislations in the future.

4.1.5. TEDX-list

The TEDX list identifies chemicals, that have been proved to be endocrine disrupting by scientific studies. TEDX researchers evaluate chemicals by searching through publicly available scientific publications and identifying peer-reviewed research that demonstrates effects on endocrine signaling.

4.1.6. The Danish Environmental Protection Agency guide to self-classifications

This guide to self-classification is intended for companies that import or produce chemicals, in the case where there is insufficient data on the hazardous properties of the chemicals. The list contains more than 54.000 indicative classifications on different compounds/chemicals and has two main purposes:

1) To help companies fulfill their requirements under the regulation of classification, labelling and packaging of substances and mixtures (CLP regulation) by self-classification of the chemical compounds and solutions they sell in the EU. ECHA must be notified of all self-classification.
2) To help companies decide whether they must make a limited registration under REACH for low tonnage compounds or if they need a full dataset. REACH, Annex III contains specific information about low tonnage compounds (1-10 ton/year), that should have been registered in 2018. For these specific compounds the information requirements in REACH, Annex VII are met if Quantitative Structure-Activity Relationships models ((Q)SAR models) or other knowledge indicate that they likely fulfill the classification criteria as carcinogenic, mutagenic or reprotoxic (CMR) or other hazardous classification combined with broad application use.

5. Assessment based on listing

An overview of the materials listed in different lists is given in Table 1. The materials were found via their CAS numbers (in some cases combined with their material names) using the online search functions of the respective lists. It is worth noting that a CAS number reflects the type of material (e.g. silver) and not the form of the material (e.g. nanoparticles). Hence a more detailed investigation of potential law documents was carried out to evaluate its relevance for the current use.

Material name	CAS- number	Candi-date list	REACH	CoRAP list	SIN-list	TED X list	DEPA self-classifica-tion
BN	10043-11-5	-	-	-	-	-	-
Graphite	7782-42-5	-	-	-	-	-	-
Ag nanoparti-cles	7440-22-4	-	-	Listed	-	Listed	-
SiO_2 nanopar-ticles	7631-86-9	-	-	Listed	-	-	-
PEEK	29658-26-2	-	-	-	-	-	-
PTFE	9002-84-0	-	-	-	-	-	-

Table 1. Table of selected materials for this environmental assessment, and an overview of the lists where they occur. If nothing is noted this means that the material was not listed in the list at the time of search (February 1st, 2022).

The severity of the listings varies widely and further details on the consequences of listing is summarized in the following sub-sections.

Regarding the listing of silver in the CoRAP list:

Silver nanoparticles have been evaluated in the Netherlands in 2014. The initial cause for concern is listed as:

- Other hazard-based concern
- High (aggregated) tonnage
- Other exposure/risk-based concern
- Wide dispersive use

The evaluation was finalized in 2018 and from the available evaluation report it was concluded that follow-up regulatory action was required at the EU level for the purposes of additional harmonized classification and labelling. The evaluation compares Ag nanoparticles to silver nitrate, $AgNO_3$, and contains the harmonized classifications of H400 and H410. The evaluation considers that Ag nanoparticles are not more harmful than $AgNO_3$. Hence the classification of H400 and H410 is considered the strictest expected outcome for the final classification of Ag nanoparticles by the evaluation report. Today both H400 and H410 are classifications for Ag nanoparticles as well. On a sperate note $AgNO_3$ has other harmonized hazard classifications.

The evaluation report further refers to future legislation actions in Europe in the form of a planned Swedish classification and labelling proposal for different forms of elemental silver and silver salts for biocidal use. This process is currently ongoing and relates to Ag nanoparticles as biocides. The current proposal status is "opinion development" with an opinion deadline on March 16th, 2022. Here Sweden has proposed the following harmonized classifications, for Ag nanoparticles used as biocide:

- H317 – May cause an allergic skin reaction.
- H341 – Suspected of causing genetic defects.
- H360Fd – May damage fertility. Suspected of damaging the unborn child.
- H400 – Very toxic to aquatic life.
- H410 – Very toxic to aquatic life with long lasting effects.

The active, Swedish proposal on harmonized classification on biocidal Ag nanoparticles has not yet been concluded but may cause further harmonized hazard classification for Ag nanoparticles in biocidal use.

Regarding the listing of SiO_2 in the CoRAP list:

The listing refers to synthetic amorphous silica (SAS) in nano-particle form. It was evaluated in the Netherlands in 2012. The initial cause for concern is listed as:

- Other hazard-based concern.
- Other exposure/risk-based concern.

The evaluation was finalized in 2018 and from the available evaluation report it was concluded that follow up regulatory action was required at the EU level for the purpose of additional harmonized classification and labelling. As a follow-up action the Netherlands plan a proposal for a harmonized classification according to Article 37(1) of the CLP Regulation. The date for this action was not decided at the time of writing.

When the Dutch evaluation report was written, no harmonized classifications were made for SiO_2, however today SiO_2 nanoparticles are classified as H332 (harmful if inhaled) and H335 (may cause respiratory irritation).

Regarding the listing of Silver in the TEDX list:

The listing refers to synthetic silver nanoparticles. It is based on a scientifically peer-reviewed paper by A. Hinther *et al.* published in "Environmental Science & Technology" in 2010. It was found that Ag nanoparticles alter the expression of genes in the cells linked to thyroid hormone action. Based on these scientific results, silver nanoparticles are listed as an endocrine disruptor.

6. Assessment based on SDS

The assessment based on SDS evaluate the hazards related to each specific material. As a specific supplier for the different materials has not been chosen at the time of writing, publicly available SDS's were used. These are listed in the appendix of this report. Where possible for each case, SDS's reflecting powders of relevant particle size were used.

The severity of a given harmonized hazard classification was evaluated on a scale from 1-5 (5 being the most severe) and the probability that this hazard is relevant in the final product was likewise evaluated on a scale form 1-5 (5 being the most likely). The product of severity and likelihood generates the overall risk-score of the material in question.

For this evaluation it was assumed that all materials would be present in an SLT in comparable amounts and that all particles would be bound in a plastic matrix, as it is the case for PTFE in the current product from CS.

Material	GHS hazard pictograms	Hazards	Severity	Probability	Risk
BN	None	None[1]	-	-	-
Graphite	None	None	-	-	-
Ag nanoparticles		H400 H410	4	3	12
SiO_2 nanoparticles		H332 H335	3	1	3
PEEK	None	None	-	-	-
PTFE	None	None	-	-	-

Table 2: Risk evaluation of hazards listed for the investigated materials. Risk is evaluated as the product of severity and probability (both scored on a scale 1-5).

[1] Boron nitride is not classified according to any harmonized hazards, but the SDS examined included the comment that dust formation of BN may lead to combustible dust concentrations in air. The SDS further advise prevention of dust accumulations to minimize the risk of explosion.

SiO_2 nanoparticles are classified as: H332 (Harmful if inhaled) and H335 (May cause respiratory irritation). These hazards are considered to have a severity of 3 on the scale of 1-5. The probability for this hazard to be relevant in the product is considered very low as the material will be present as particles bound in a plastic matrix. As such, the hazard is only relevant for the employees involved in the production of the SLT at CeramicSpeed, while it is not considered relevant for the end user of the SLT.

Ag nanoparticles are classified as H400 (very toxic to aquatic life) and H410 (very toxic to aquatic life with long lasting effects). This was considered to have a severity of 4 because of the large effects on the environment. The probability for this hazard was given a score of 3 as parts of products that undergo wear have a risk of eventually ending up in the environment. Furthermore, the presence of Ag nanoparticles in the SLT will increase the handling responsibility for worn-out bearings. It should be further noted that silver nanoparticles are marked with the precautionary statement P273 (avoid release to the environment).

7. Limitations of assessment

This environmental and health assessment is based on publicly available data, material listings, and SDS's of representative materials. For the evaluation in this environmental and health assessment the materials are evaluated in their pure form, hence this information does not consider if the material chemically reacts with surroundings in the form of which it is used. Furthermore, the material listings are based on the material type and not the form of the material. By further investigation of the case documents of the specific listings for Ag and SiO_2, it was found that these reflected specific concerns related to powder or nanoparticle forms of the materials.

Some of the materials evaluated, especially PEEK, are not widely used as powders, nor are they widely used for purposes similar to the role of the material in an SLT. Therefore, not all the materials have undergone a thorough scientific investigation to evaluate the safety of the specific powder form, as it has been the case for Ag and SiO_2 nanoparticles. Hence, it is possible that unwanted effects of material powders could be found in further investigations for the specific form and use, however this is not considered likely.

The assessment carried out in this report assumes that one would use the same amounts of material in the SLT and that all materials are bound in a plastic matrix without chemically reacting with the matrix. It has been assumed that the materials will remain bound in the matrix for all cases, however no experimental studies have been conducted to verify this.

The disposal of worn-out materials should be considered in the final product evaluation. This includes but is not limited to the evaluation of whether the plastic matrix (including the additives) can be recycled or if the plastic matrix and all contents have to be disposed of via combustion. The environmental and health evaluation does not consider if the materials are approved as food contact material in the given form.

Appendix A: References

Lists:

Candidate list: https://echa.europa.eu/substances-of-very-high-concern-identification-explained

CoRAP list: https://echa.europa.eu/information-on-chemicals/evaluation/community-rolling-action-plan/corap-table

REACH: https://echa.europa.eu/en/substances-restricted-under-reach

SIN-list: https://sinlist.chemsec.org/

TEDX list: http://endocrinedisruption.org/

The Danish Environmental Protection Agency guide to self-classifications; https://eng.mst.dk/chemicals/chemicals-in-products/assessment-of-chemicals/the-advisory-list-for-self-classification-of-hazardous-substances/

SDS's:

Product-type	Supplier and product name	Revision date of SDS
Boron Nitride	Saint-Gobain, Boron Nitride Powders	07.04.2021
Graphite:	Supelco (Sigma Aldrich). Graphite fine powder extra pure, Product number: 1.04206	13.03.2021
Silver nanoparticles:	Sigma-Aldrich, Silver, product number: 484059	06.02.2020
PEEK:	Aldrich, Polyetheretherketone (PEEK), powder, mean particle size 80micron, Product number: GF75065755	14.06.2019
SiO_2	Skyspring Nanomaterials, Inc, Silicon oxide nanopowder	02.01.2016
PTFE	SDS from Biesterfeld ULTRAFLON MP-8T	21.08.2017

Other references:

Swedish harmonized classification proposal: https://echa.europa.eu/da/registry-of-clh-intentions-until-outcome/-/dislist/details/0b0236e183963736

Five European states call for evidence on broad PFAS restriction: https://echa.europa.eu/da/-/five-european-states-call-for-evidence-on-broad-pfas-restriction

Paper for TEDX list:

Hinther A, Vawda S, Skirrow RC, Veldhoen N, Collins P, Cullen JT, van Aggelen G, Helbing CC. 2010. Nanometals induce stress and alter thyroid hormone action in amphibia at or below North American water quality guidelines. Environ Sci Technol 44(21):8314-8321. DOI: 10.1021/es101902n.

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