Request for derogation on the use of PTFE as anti-drip agent in thin wall flame retardant polycarbonate compounds

Table of Contents

Executive Summary

Flame retardant polycarbonate compounds used in thin-wall consumer electronics applications plays a critical role in consumer safety and requires the use of PTFE as an anti-drip additive. Thin walled parts reduce the amount of plastic used and therefore the amount of plastic waste produced during the manufacturing process as well as at the electronic devices' end of life. Before these tough thin-wall flame retardant polycarbonates were available, typical wall thicknesses in consumer electronics were 2-3 mm, which in comparison can lead to a 100% to 200% increase in resources consumption and solid waste generation, depending upon the electronic application design requirements. Thin-walled polycarbonate can also lead to lighter products which require less energy for transportation, resulting in less CO_2 emissions.

Our justification for requesting derogation of PTFE as anti-drip agent in flame retardant polycarbonate compounds comprises two elements:

- there are no alternatives to polycarbonate that provide adequate impact resistance and ductility for thin wall (<=1.5mm) applications in electronic products
- in order to ensure that the polycarbonate thin wall has adequate flame retardancy, it is essential to use PTFE as the anti-drip agent

There is no other engineering plastic available today which provides adequate levels of impact resistance and ductility compared to polycarbonate. These properties are crucial to:

- provide a durable product that does not break during normal use, including drops and other foreseeable events
- ensure safety by avoiding exposure of life circuitry, and
- meet EU regulatory requirements on the safety of electrical device

The next best material is polyphenylsulfone (PPSU) which has almost half the ductility. By extension, we can expect that electronic products with thin walls (<=1.5mm) made from PPSU would be twice as fragile compared to the same products made with polycarbonate. Increased fragility means increased risk that the device may break after an impact event, which may result in electrical hazard (short circuit, shock hazard) or fire hazard.

We have carried out a thorough analysis of the latest available flame-retardant and anti-dripping technology for polycarbonate, via a patent and literature review, as well as our own in-house technical expertise based on decades of experience with plastics. Our review of patents found that most flame-retardant polycarbonate materials are formulated with PTFE as an anti-dripping agent. We did find some patents which do not use PTFE; however, we did not find any non-PFAS alternatives which are acceptable from the standpoint of environment and human health, and which do not compromise the impact resistance and ductility of the polycarbonate. Our literature review found that all recently developed flame retardants mandate the use PTFE as an anti-drip agent in polycarbonate.

Our company has also carried out our own in-house experiments to investigate whether we could develop alternative additives that could be used instead of PTFE. None of the alternatives that we tested was able to provide adequate flame-retardant properties without significantly degrading impact resistance or other mechanical properties.

1. Introduction to thin wall flame retardant polycarbonate

Injection mouldable polycarbonate resins, polycarbonate blends and polycarbonate copolymer resins are used for thin wall flame resistant enclosures, structural components and/or insulators for the consumer electronics industry. Thin-walled parts produced from these types of polycarbonate resins reduce the amount of plastic used and therefore the amount of plastic waste produced during the manufacturing process as well as at the electronic devices' end of life. Before these tough thin wall flame retardant polycarbonates were available, typical wall thicknesses in consumer electronics were 2-3 mm, which in comparison can lead to a 100% to 200% increase in resource consumption and solid waste generation, depending upon the electronic application design requirements. Thin-walled polycarbonate can also lead to lighter products which require less energy for transportation, which results in less CO_2 emissions.

Flame retardant polycarbonate is provides an extraordinary combination of mechanical, electrical, and flammability properties and has become increasingly used in almost every electronic device. Electronic devices often rely on unique combinations of properties that polycarbonates can have, including mechanical/impact strength, electrical insulation, flame resistance, corrosion resistance, integral (no-paint) color, and weather resistance. Depending upon the end use application, any combination of these properties could be the deciding factor for using polycarbonates versus other thermoplastic materials. For instance, consumer electronics often need lightweight, molded-in functionality with impact, electrical, and flame resistance that alternate thermoplastic materials cannot meet.

2. Analysis of alternatives for polycarbonate in electronic products

For thin (<=1.5mm) injection moulded walls in electronic products, along with fire resistance, impact resistance and ductility are essential requirements. Impact resistance is measured using the Notched Izod impact strength test (ASTM **D256-10(2018)** standard method[1]). Ductility is measured using elongation at break testing which measures how much a material can be stretched, as a percentage of its original dimensions, before it breaks[2].

As highlighted in the table below, polycarbonate offers unmatched impact resistance and ductility compared to other engineering plastics, which is crucial to:

- provide a durable product that does not break during normal use
- ensure safety by avoiding exposure of life circuitry, and
- meet EU regulatory requirements of the electrical device.

	Impact resistance	Ductility
	Notched Izod strength relative to polycarbonate	Elongation at break relative to polycarbonate
Polycarbonate	100%	100%
ABS	48%	23%
Nylon	7%	66%
Polyphenylsulfone (PPSU)	83%	55%
Polystyrene (PS)	17%	38%
Polyethylene terephthalate (PET)	4%	51%

[1] https://www.astm.org/d0256-10r18.html

[2] https://www.curbellplastics.com/Research-Solutions/Plastic-Properties

Poly (methyl methacrylate) (PMMA)	3%	3%
Polyether ether ketone (PEEK)	10%	44%

Additional considerations:

- Nylon: in addition to inferior impact resistance and ductility, nylon contains hydrophilic amide groups which makes nylon water-absorbent and causes it to expand. Water absorption results in dimensional changes to the plastic part which can cause the product to fail safety testing.
- PMMA: PMMA is infrared transparent and is often used in applications requiring infrared remote-control features. However, PMMA is more brittle than polycarbonate, which limits its application for electronic industry.
- PEI and PEEK: the impact performance is about 20 times lower than polycarbonate.
- Thermal stability is important for some applications where heat may be generated during operation of the electronic product. Polycarbonate has excellent thermal stability, while plastic like PBT have poor thermal stability, making them unsuitable for those applications.

In conclusion, there are no alternatives to polycarbonate that provide adequate impact resistance and ductility for thin wall (<=1.5mm) applications in electronic products.

3. Analysis of alternatives for PTFE as an anti-dripping agent in polycarbonate

It would be unacceptable and unsafe to use polycarbonate without an anti-dripping agent to prevent the spread of fire. Doing so could create fire hazards and would not allow products to comply to mandatory fire safety standards. PTFE is currently the anti-dripping agent in polycarbonate in electronic products. The high shear forces in the injection moulding process cause the PTFE to stretch and form fibrillated structures in the polycarbonate. Due to the high thermal stability of PTFE, the fibrillated structure remains intact during combustion process and forms a char which prevents dripping of burning plastic. PTFE also contributes to improved impact resistance and ductility.

We have carried out a thorough analysis of the latest available flame-retardant and anti-dripping technology, via a patent and literature review. Our review of patents found that most flame-retardant polycarbonate materials are formulated with PTFE as an anti-dripping agent. We did find some patents which do not use PTFE; however, we did not find any non-PFAS alternatives which are acceptable from the standpoint of environment and human health, and which do not degrade the impact resistance and ductility of the polycarbonate.

Additive/Technology	**Observation**	**Conclusion**
0.1%-0.5% potassium perfluorobutane sulfonate (KFPBS)[1]	KFPBS is a PFAS.	KFPBS is a PFAS and would therefore also be banned from use without a derogation
20% phosphorus-based flame retardant[2]	Significant reduction of impact resistance, ductility and thermal properties.	As the polycarbonate will not meet the mechanical properties required by the EU safety standards, this material cannot be considered as an acceptable alternative
Aromatic brominated flame retardants[3]	The Regulatory Strategy for Flame Retardants published March 2023[3] proposes to ban the use of aromatic brominated flame retardants.	Due to enacted and proposed regulatory restrictions this material cannot be considered as an acceptable alternative

[3] https://echa.europa.eu/documents/10162/2082415/flame_retardants_strategy_en.pdf/9dd56b7e-4b62-e31b-712f-16cc51d0e724?t=1678871526283

	The WEEE directive requires selective treatment for plastic containing brominated flame retardants. Ecodesign requirements for electronic displays forbid the use of halogenated (including brominated) flame retardants in the enclosure and stand of electronic displays.	

Patent References: [1] EP4021978A1, [2] US20210171766A1, [3] CN112745641B

We have carried out an extensive literature review to investigate whether there are any new flame retardants recently developed that may not require the use of PTFE. Our review has found that all recently developed flame retardants mandate the use PTFE as an anti-drip agent.

FR Additive	Observation	Conclusion
Polyphenylsilsesquioxanes (cyc-PPSQ)[4]	0.3% PTFE is added as an anti-dripping agent to meet flame retardant standards	This new flame retardant still requires the use of PTFE
Silicon-phosphorus linear polymer[5]	0.45% PTFE is added as an anti-dripping agent to meet flame retardant standards	This new flame retardant still requires the use of PTFE
Expandable graphite[6]	PTFE is added as an anti-dripping agent to meet flame retardant standards	This new flame retardant still requires the use of PTFE

Literature References: [1] Journal of Materials Science 55 (2020): 10953-10967[2], Fire and Materials 43 (2019): 685-693, [3] Materials & Design 214 (2022): 110419

Our company has also carried out our own in-house experiments to investigate whether we could develop alternative additives that could be used instead of PTFE. Our research is summarised below. None of the alternatives that we tested was able to provide adequate flame-retardant properties without significantly degrading impact resistance or other mechanical properties.

The results of our in-house experiments on anti-drip agents are presented in the below tabular format. These chemicals were selected for experimentation as the most promising potential alternatives based on our own in-house expertise and literature and patent searching. As explained below, based on our experimental results, none represents an acceptable alternative to PTFE.

Tested technology	CAS#	Experimental result	Conclusion
Talc-based	Trade secret	Burning drips developed during flammability testing Significant reduction of mechanical properties	Does not provide adequate flame retardant properties
Sufur-based	Trade secret	Burning drips developed during flammability testing	Does not provide adequate flame retardant properties
Silicone-based	Trade secret	Burning drips developed during flammability testing	Does not provide adequate flame retardant properties
Boron-based	Trade secret	Burning drips developed during flammability testing Significant polymer degradation.	Does not provide adequate flame retardant properties. Additionally, it is an SVHC which would be a regrettable substitution
Phosphorus-based	Trade secret	Significant reduction of impact resistance, ductility, and thermal properties.	As the polycarbonate will not meet the mechanical properties required by the EU safety

[4] Journal of Materials Science 55 (2020): 10953-10967

[5] Fire and Materials 43 (2019): 685-693

[6] Materials & Design 214 (2022): 110419

			standards, this material cannot be considered as an acceptable alternative

In the Regulatory Strategy for Flame Retardants[7], ECHA also acknowledges that fluoropolymers, especially high molecular weight (HMW) PTFE, provide flame retardancy to polymers used in various industrial applications. PTFE, when incorporated into the polymer compound, reduces the dripping of the polymer upon burning and thereby retards the spread of flames. PTFE is added with loadings up to 0.5 wt%.

4. Proposed text for derogation for Thin Wall Flame Retardant Polycarbonate

There are no alternatives to PTFE available today for thin wall flame retardant polycarbonate. A wide range of potential alternatives have already been tested and found to fail to provide the necessary properties. A new round of extensive, fundamental laboratory research will be needed to attempt to identify a completely new material, unknown today, that may potentially be developed into an alternative to PTFE. We expect it may take up to 8 years to carry out this basic research.

If a new alternative material is identified it would take several more years to test, qualify, certify, and start manufacturing parts from this replacement material. Companies may need to make changes to their manufacturing equipment and processes to use the new material in their injection moulding lines. These changes to manufacturing equipment and processes may be significant and require extensive time and capital investment.

Product requalification is a very time-consuming exercise which will require extensive resources over many years. The completion of this task will require sufficient test house capacity and transition time to requalify all existing thin wall flame retardant polycarbonate parts in products which are used in Europe for safety and performance. For a company with a wide range of existing product designs, we estimate it could take up to 5 years to carry out the necessary manufacturing equipment changes and product re-qualifications.

In view of this, we recommend a minimum 13.5 year derogation for flame retardant polycarbonate compounds for the production of thin walled parts, as follows:

By way of derogation, paragraphs 1 and 2 shall not apply to: **[xx] flame retardant polycarbonate for the production of thin walled parts until 13.5 years after EiF**

5. Critical Safety Need for Flame Retardants in Electronics

Statistics from several European countries reveal that electrical equipment account for 25 - 30% of all domestic fires, estimated in 273,000 fires per year. Fires can be generated by

[7] Materials & Design 214 (2022): 110419

devices connected to the mains power, or battery powered devices. Lithium-ion batteries, in a fault condition, are also capable of overheating leading to ignition and subsequent explosion.[8]

Flame retardancy has been proven to work and continues to be a powerful tool in the overall efforts to prevent fire related injuries and save lives. One of the most important benefits of flame retardancy in product design is they can stop small ignition events from turning into larger fires. Even if ignited material with flame retardancy also delay the spread of fire to give people sufficient time to escape. For example in the EU, due to the introduction of increased fire safety standards — the number of fire victims fell by more than 48% in France from 1982 to 2012, and by 56% in the UK from 1982 to 2013. Overall Europe has achieved substantial improvements in fire safety, with fire fatalities dropping by 65% over the last 30 years[9]. Since 2017, nearly different 500 types of electronic products have been recalled, withdrawn, or banned from sale in the EU due to fire hazards[10].

Other materials and components used in electronics are insufficient to prevent or delay the spread of fire from electronics. For example, protective components within electronics can reduce but not eliminate the risk of fire from electrical malfunction/failures. For example, a thermal fuse in a motor operated appliance will offer protection against an abnormal overload condition but it will not protect against other component failures like overheated power switches, connectors, wiring etc.

Another example is current-limiting components such as circuit breakers that are triggered by current rather than voltage. Once they are triggered, current limiting devices restrict power from reaching the equipment being protected without having to dissipate that power as heat. Therefore, there is virtually no limit to the amount of energy that they can handle. However, current-limiting devices do not generally respond fast enough to protect equipment from fast transient overvoltage's generated by lightning or electrostatic discharge which can lead to a flashover/arcing.

It is therefore essential to continue to guarantee the availability of PTFE and flame-retardant polycarbonate for the safety of electrical equipment on the European market until an effective and safe alternative can be found.

6. EU regulatory requirements for flame retardants

Polycarbonate with flame retardancy is used especially in electrical and electronic equipment including IT applications, household appliances such as a hair dryer, adapters, charger, notebook computer, smart meters, lighting applications, and charging stations for electric vehicles. Polycarbonate is selected due to its unique combination of properties including fire retardancy, heat resistance, dimensional stability and impact resistance, which are critical to the ensure the safety of the final application (e.g., prevent electrical shocks).

The European low voltage directive (2014/35/EU) sets safety requirements for electrical equipment within certain voltage limits. Those safety requirements are defined by the EN 60335-series standard, which includes stringent flammability requirements.

Standards EN 60695-11-10 (test flames methods, ignition source with a nominal thermal power of 50 W) defines the burning classification of plastics materials. The flame behaviour of plastic materials is described as their ability to burn / extinguish and spread fire. V-0 materials are the highest flame-retardant class (most flame-retardant), offering the highest protection against fire hazard. Materials classified as V-0 shall not burn (burning stops within 10 seconds

[9] Modern building alliance Europe: Fire Death Rate Trends: An International perspective

[10] Safety Gate: the EU rapid alert system for dangerous non-food products

on a vertical specimen) and shall not spread fire (drips of particles are allowed as long as they are not inflamed). Materials classified as V-1 (the second highest flame-retardant class) shall stop burning within 30 seconds on a vertical specimen, and drips of particles shall not be inflamed. Similarly, according to standard EN 60695-11-20 (test flames methods, ignition source with a nominal thermal power of 500 W), to be rated 5VA, a material must stop burning within 60 seconds on a vertical specimen, no drips are allowed, and the plaque specimens may not develop a hole. 5VB rated materials must stop burning within 60 seconds on a vertical specimen, no drips are allowed, and the plaque specimens may develop a hole.

In order to achieve compliance with those standards, flame retardant additives, to stop the burning, and anti-dripping additives, to prevent fire spreading, are included in the formulation of V-0, V-1, 5VA and 5VB rated materials. The role of PTFE in flame retardant polycarbonate is to prevent the formation of dripping particles, and therefore ultimately to prevent a fire from spreading.

7. Socio-economic impacts

The Electrical and Electronics (E&E) sector represents the second largest market for polycarbonate in the EU. In 2015, 23 % (147,200 t) of the total polycarbonate consumption in the EU (ca. 640,000 t*) was used to make products in the E&E-sector. Polycarbonate helps manufacturers meet the need for continuously higher standards of appearance, sustainability and safety, and satisfying emerging regulatory and eco-design standards. In 2010, the total European E&E sector supported 26 million jobs and generated value added of € 139 billion, of which polycarbonate applications made as substantial contribution. Together with applications in the domestic appliances/household sector which consumed 8% (51,200t), these two market sectors account for nearly one third of all polycarbonate consumption in the EU.

Besides being the material of choice to meet the regulatory requirements in E&E sector, polycarbonate is also used in automotive, aircraft, railway, construction, and many other applications, due to its unique combination of characteristics.

Please refer to the confidential Annex for additional information.

8. PFAS tonnages and releases from flame retardant polycarbonate

Please refer to the confidential Annex for information on our uses.

PTFE is ‘encapsulated’ into the polymer matrix, and it is not expected to migrate or leach out of polycarbonate during service life of the products.

Directive 2012/19/EU on Waste from Electrical and Electronic Equipment (WEEE) regulates the end of life of electrical and electronic equipment and sets targets for the separate collection and recovery and recycling of this equipment, and the proper treatment of residual un-recycled fractions. In view of this, it is not expected that PTFE used in polycarbonate will make significant contribution to the releases of PFAS in the environment.

Appendix 1: Literature review references and patent review references

1. Yan, C., Xu, B., Shan, D., Zhang, W., Xu, Y., Chen, Y., ... & Liu, L. (2023). Fabrication and mechanism research of high-efficiency water-resistant flame retardant, transparent and mechanically reinforced polycarbonate composites. *Polymer Testing*, *119*, 107937.
2. Amirabadi, S., Kakroodi, A. R., Dias, O. A. T., Sain, M., & Park, C. B. (2022). Tailoring nano-fibrillated polystyrene composite with enhanced fire retarding properties for foam applications. *Materials & Design*, *214*, 110419.
3. Wu, X., Qin, Z., Zhang, W., Guo, X., Pan, Y. T., & Yang, R. (2020). Halogen-free and phosphorus-free flame-retarded polycarbonate using cyclic polyphenylsilsesquioxanes. *Journal of Materials Science*, *55*, 10953-10967.
4. Song, W., Zhang, W., Li, Y., Ma, H., Lin, T., Lu, C., ... & Chen, Z. (2019). Construction of novel silicon-phosphorus linear polymers with DDSQ and DOPO derivatives for effective flame retardancy of PC/ABS. *Fire and Materials*, *43*(6), 685-693.
5. Jiang, J., Wang, Y., Luo, Z., Qi, T., Qiao, Y., Zou, M., & Wang, B. (2019). Design and application of highly efficient flame retardants for polycarbonate combining the advantages of cyclotriphosphazene and silicone oil. *Polymers*, *11*(7), 1155.
6. Gelmont, M., Yuzefovitch, M., Yoffe, D., Eden, E., & Levchik, S. (2020). Alkylation of aromatic compounds with pentabromobenzyl bromide and tetrabromoxylene dibromide as a new route to high molecular weight brominated flame retardants. *Polymers*, *12*(2), 352.

JP2020189942A	CN112480637A	JP2021024877A	JP07218085B2
JP2020111668A	CN113278275A	JP2022070453A	HK40031529A
US20220112369A1	CN106398096A	WO2020100727A1	US20200277491A1
EP3858919A1	CN104693735A	WO2022097449A1	CN114716812A
EP3858919A4	CN104710743A	CN112236478A	CN115029833A
WO2020066535A1	CN104710738A	JP2022066647A	KR2494931B1
CN112752797B	CN101134839B	JP2021024878A	CN112442072A
CN112752797A	CN104693772A	WO2021020095A1	CN111534885A
JP06976453B2	CN111019179A	WO2021020094A1	IN202017020163A
TW202026359A	CN110591326A	JP2021024876A	EP3480255A4
JP07072589B2	CN102863749A	JP2022142246A	CN112300570B
JP2022147096A	CN104672838A	US20210388140A1	WO2020184270A1
EP3247742B1	CN104629308A	EP4098691A1	WO2020184839A1
CN107207863B	CN110093023A	WO2020004046A1	IL251442A
TWI691552B	CN107828202A	JP2021014478A	KR2021089896A
JP2020066710A	CN103772954A	JP2020105433A	CN115182068A
CN111073248A	CN104845333A	JP06904173B2	WO2021205938A1
JP2020189944A	CN111286163A	JP2022040551A	IN345073B
JP2022097753A	CN100346051C	JP2020203963A	CN112480398A
WO2021233774A1	US7728059B2	JP07174602B2	JP07181789B2
CN115516035A	CN103772949A	CN114656760A	CN114196196A
EP3560997A4	CN103360735B	US20220325037A1	WO2022191078A1
WO2022045616A1	CN104845315A	CN112745641B	CN112795183B
KR2022028623A	CN105062031A	WO2021253771A1	CN114957977A
KR2200871B1	NL197713813A	JP07075317B2	CN113174089A

EP3733772A1	CN101875767B	CN105926068A	EP2252653B1
EP3733772A4	CN106084576A	CN105111706A	EP3700976B1
US20200283624A1	IT1166576B	JP5117513A	CN109020798B
EP3733770A1	JP2017226767A	US8557158B2	CN113549402B
EP3733770A4	US20120220709A1	KR1622882B1	IN202227020510A
CN111615538A	CN108504069B	CN107793731A	CN104559107A
JP2021509125A	US7687567B2	CN104650571A	CN109233111A
US11124647B2	CN101619161B	US4147707A	CN105038178B
EP3564314A4	CN103772941B	CN105924736A	KR2019078391A
US10822493B2	US9718956B2	US9688854B2	US7208542B2
CN109988406B	KR1776990B1	JP5279562A	RU159582U1
JP2023012167A	US9056978B2	KR342105B1	CN105086406B
US11208553B2	CN101875768B	US10100196B2	CN106633747A
CN112538252A	CN102675849A	KR2297673B1	CN107892837B
CN112375359A	CN105542422A	IN201617014927A	CN106867225A
CN104479319A	CN107177180A	CN103738046A	CN101875772B
CN103772921B	WO2021200841A1	JP2007077334A	CN114350121A
CN102690507B	JP6041415A	CN108148298A	CN114369352A
CN111269548B	CN206703482U	CN104861371A	WO2021036614A1
CN103772946A	CN113621150A	CN108148373A	CN113861654A
CN106147192A	CN113698750A	CN103205092A	EP4011977A1
CN114230891A	WO2016175604A1	JP2008230949A	CN114525026A
CN107057319A	US9365720B2	JP2015224321A	CN102585476B
CN109941068A	CN113558356A	CN105504738A	CN110041668A
CN103881332A	WO2015008831A1	CN111764006A	CN110204880A
CN107141718A	KR1990162B1	JP05040644B2	CN105802181A
CN111019314A	KR2017092143A	JP2000086854A	CN104788929A
CN103602051A	CN101851407B	JP2019199490A	US20140275366A1
CN103709708A	CN107082586A	CN103302927A	CN106479148A
CN104725820A	JP2013103981A	CN110128809A	CN104672849A
CN105153662B	CN101538403A	IN201202210P3	CN104419180A
CN104277440A	CN105694410B	CN108610595A	TW202112962A
CN104497523A	CN112876830A	CN106009552A	CN107674399A
CN104672846A	WO2022057204A1	JP7258531A	CN213449132U
CN204005729U	US9969876B2	CN108659495B	EP2955201A1
KR1221690B1	US5326793A	CN102604353B	CN107541037A
JP2010059316A	EP2138291B1	CN111484719A	CN104072965A
US20150322261A1	CN104194284A	CN103408909B	CN104072964A
CN107868429A	CN213184308U	CN102850745A	CN105670288A
JP2014205591A	CN105694205B	CN113429773A	CN104031373A
WO2014088105A1	CN102558699A	CN105949612A	CN104031371A

JP06239960B2	JP05365265B2	CN104371293B	CN109749385A
EP2597120A1	CN105060738B	WO2021036612A1	CN102898801A
WO2020197132A1	CN106189758B	CN104672841A	CN104962055A
JP2007114264A	CN103571046A	CN103265801B	CN111117185A
WO2015046441A1	JP4006127A	CN103342884B	CN104419190A
EP1802696B1	JP2012102287A	CN114316560A	CN111875944A
JP06436768B2	JP3273052A	CN110684334B	CN106893299A
CN106751652B	CN106700470A	CN104341754A	JP2018141047A
CN105331025A	CN107964237A	CN104356625A	CN105331075A
RU152873U1	CN210190791U	CN111607210A	CN104419172A
CN104647678A	JP04666459B2	CN103408915B	CN108148386A
CN106336642A	GB2165253A	CN103709711A	CN104910601B
CN104629289A	CN101722635A	CN103740078A	CN103724963B
CN104650563A	JP9290482A	CN103408908A	CN103182818B
CN107118533A	GB2138826A	CN107868428A	CN106433065A
CN111040411A	KR1481217B1	CN104119665A	CN104140662A
ZA198707297B	EP2895555A1	CN106633778A	CN111484722A
CN108059810A	EP2895556A1	CN104672883A	CN104693763A
CN104710754A	CN108997656A	CN104650554A	CN106147121B
FR3041283A3	JP04971544B2	CN104497532A	US5175198A
KR2023015342A	WO2018050659A2	CN112980152A	CN107278219B
WO2021233773A1	KR2014494B1	JP06663292B2	WO2020153330A1
CN115551945A	CN103408835B	CN112724619A	BR112012005734A2
KR2023014692A	CN103214801B	WO2022110663A1	KR2244041B1
CN115362213A	CN106995569A	CN112778731A	CN108559256B
KR2022161299A	US4113692A	EP694582A2	CN109306176B
US11352478B2	CN101350261B	CN105820539A	WO2022214754A1
US20200010641A1	CN111704792A	JP2019206650A	TW202237744A
CN110402270B	CN103881346A	WO2020054223A1	CN114729186A
JP07109420B2	DE2756925A1	CN105713364A	WO2022158383A1
JP2021038298A	CN113150527A	JP2002309076A	KR2023025383A
JP2020037632A	JP2016084454A	KR2013089340A	WO2022077865A1
CN107075140B	JP55019944B2	US20200086539A1	IN401832B
CN112189033A	CN103589123A	CN105694414A	WO2020243991A1
JP07069306B2	CN113372706A	JP2008239940A	CN112457343A
TW202006063A	CN112812532A	US5807914A	CN112375377A
CN112708253A	CN114479408A	KR1159635B1	EP3530698B1
CN115703926A	US10642071B2	CN103254577A	WO2021257531A1
JP06837336B2	CN106751642A	CN207106631U	WO2021134733A1
JP06836246B2	CN109575554A	CN103724965A	WO2021044880A1
KR2204271B1	JP54094556A	CN106995598A	CN113072807A
CN109486147B	FR2936831A1	CN103013089B	CN113354867A

US20220267596A1	JP4089859A	KR2087405B1	KR2164977B1
WO2021037705A1	CN106810841A	CN107298837A	CN111471183A
CN111675891A	EP16058A1	CN102850753A	EP4069757A1
WO2021228636A1	TH165272A	CN102382440B	EP3564319A4
CN115461408A	US20180291197A1	CN102181139B	KR2499710B1
KR2023009892A	CN104693767A	JP06652332B2	EP3858888A1
KR2021106846A	US8829086B2	CN111154246A	JP07093104B2
CN114736500A	KR1348534B1	US20020135161A1	WO2022231250A1
JP07011899B2	WO2014115475A1	CN202202478U	CN114621586A
CN112778741B	CN102658656A	CN105462223B	CN214406735U
CN112778741A	KR2015067740A	CN103509219A	CN107189098B
CN112824450A	CN107722587A	CN103525060B	KR2021047256A
US20210171766A1	US20140050815A1	JP05617245B2	CN113150382A
EP3733772B1	CN101875770B	US4048133A	JP2020122098A
CN106393894A	CN104629288A	CN107400276A	