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- as to the applicant's entitlement to claim the priority of the earlier application (Rule 4.17(iii))

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(54) Title: CURABLE FLUOROELASTOMER COMPOSITIONS CONTAINING AMMONIUM HYDROXYBENZOATE CATALYSTS

(57) Abstract: Compositions comprising an uncured highly fluorinated elastomer comprising nitrile groups and ammonium hydroxybenzoate catalysts that can be used to cure the nitrile-group containing fluoropolymers are described. Cured compositions are also described.

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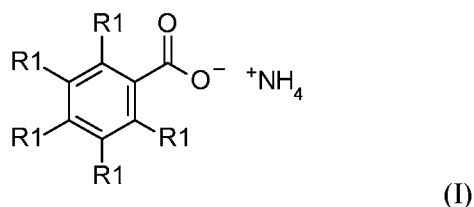
CURABLE FLUOROELASTOMER COMPOSITIONS CONTAINING AMMONIUM HYDROXYBENZOATE CATALYSTS

FIELD

[0001] The present disclosure relates to curable fluoroelastomer compositions containing compounds having an ammonium cation and an anion comprising a hydroxybenzoate. The use of such compounds as catalysts for perfluoroelastomers containing nitrile cure site groups and cured compositions are also described.

SUMMARY

[0002] Briefly, in one aspect, the present disclosure provides compositions comprising an uncured highly fluorinated elastomer comprising nitrile groups and an ammonium hydroxybenzoate compound according to Formula (I)



wherein each R1 group is independently selected from the group consisting of H, OH, R and OR, wherein each R is an alkyl group, provided that at least one R1 group is OH.

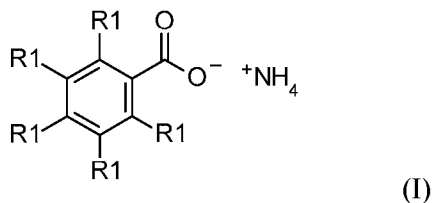
[0003] In other aspects, the present disclosure provides cured elastomers prepared from such compositions, including articles comprising cured elastomers.

DETAILED DESCRIPTION

[0004] Fluoroelastomers, particularly perfluorinated elastomers, can have excellent solvent and temperature resistance. Fluoroelastomers have been cured by a wide variety of mechanisms including the use of cure site monomers and a corresponding catalyst, sometime referred to as a curative. For example, peroxide curing systems have been used with bromine- and iodine-containing cure site monomers.

[0005] In high temperature applications, nitrile-containing cure site monomers have been used. In some cases, onium catalysts have been used to cure such perfluoroelastomers. Commonly used onium catalysts include a low molecular weight fluorinated or perfluorinated anion. It was believed that these fluorinated anions were required to achieve the compatibility with highly fluorinated elastomers needed to allow them to act as effective crosslinking catalysts. Surprisingly, the present inventors discovered that the non-fluorinated ammonium hydroxybenzoate compounds of the present disclosure are compatible with highly fluorinated elastomers and can provide curing properties comparable to the traditional fluorinated onium catalysts. Also, in some embodiments, the hydroxybenzoate compounds of the present disclosure can provide improved compression set at high temperatures, improved scorch resistance, or both, as compared to other fluorinated and non-fluorinated onium catalysts.

[0006] Generally, the non-fluorinated ammonium compounds of the present disclosure are low molecular weight ammonium hydroxybenzoate compounds. As used herein, a hydroxybenzoate is benzoate derivative substituted by one or more hydroxy groups in any position on the benzene ring, as shown in Formula (I)



wherein at least one R1 is OH. In some embodiments, each R1 is independently H or OH. In some embodiments, one or more R1 groups may be an alkyl group or an alkoxy group, e.g., a C1 to C4 alkyl or alkoxy group.

[0007] In some embodiments, the anion may be a monohydroxybenzoate such as the anion of 2-hydroxybenzoic acid (also referred to as salicylic acid) or 4-hydroxybenzoic acid. In some embodiments, the benzoate anion may be substituted with two or more hydroxy groups. For example, in some embodiments, the anion may be a trihydroxybenzoate such as the anion of 3,4,5-trihydroxybenzoic acid (also referred to as gallic acid). In some embodiments, the anion may include one or more substituents other than hydroxy groups. For example, in some embodiments, the anion may be a hydroxy-alkyl or hydroxy-alkoxy benzoate such as the anion of 4-hydroxy-3-methoxybenzoic acid (also referred to as vanillic acid).

[0008] The present inventors discovered that, despite using a non-fluorinated anion, these ammonium hydroxybenzoate compounds are compatible with highly fluorinated elastomers.

[0009] As used herein, a “highly fluorinated” polymer is one in which at least 80 mole%, e.g., at least 90 or even at least 95 mole% of the hydrogen atoms of the polymer backbone have been replaced with fluorine atoms. In some embodiments, 0 to 20 mole%, e.g., 5 to 15 mole% of the hydrogen atoms of the polymer backbone may be replaced with chlorine atoms. In some embodiments, these highly fluorinated polymers may include one or more hydrogen-containing end groups or pendant groups, which are not considered to be part of the polymer backbone.

[0010] In some embodiments, the highly fluorinated elastomer is a copolymer of tetrafluoroethylene (TFE) and one or more perfluorinated comonomers. In some embodiments, at least one perfluorinated comonomer is a perfluoroalkylvinyl ether (PAVE), including perfluoroalkyl alkoxy vinyl ethers. Suitable PAVEs include perfluoromethyl vinyl ether (PMVE), perfluoroethyl vinyl ether (PEVE), and perfluoropropyl vinyl ether (PPVE-1 and PPVE-2). In some embodiments, at least one perfluorinated comonomer is a perfluoroalkyl allyl ether (PAAE), including perfluoroalkyl alkoxy allyl ethers. Suitable PAAEs include perfluoromethyl allyl ether (MA-1), perfluoroethyl allyl ether (MA-2), and perfluoropropyl allyl ether (MA-3).

[0011] In some embodiments, at least one perfluorinated comonomer is a perfluorinated alpha-olefin other than TFE, such as hexafluoropropylene (HFP). Additional optional comonomers include partially

fluorinated alpha olefins (e.g., $\text{CH}_2=\text{CF}_2$, VDF), F and Cl containing olefins such as chlorotrifluoroethylene, and non-fluorinated alpha olefins such as ethylene or propylene.

[0012] In some embodiments, the polymer is a perfluorinated, i.e., at least 99 mole% or even 100 mole% of the hydrogen atoms of the polymer backbone have been replaced with fluorine or chlorine atoms, preferably fluorine atoms. If chlorine atoms are present, they comprise no greater than 20 mole%, e.g., no greater than 10 mole% based on the total moles of fluorine and chlorine atoms on the polymer backbone. In some embodiments, the perfluorinated polymer comprises no greater than 5 mol%, e.g., no greater than 1 mole%, or even no greater than 0.01 mole% chlorine atoms based on the total moles of fluorine and chlorine atoms on the polymer backbone.

[0013] Generally, the highly fluorinated elastomer contains a sufficient number of nitrile groups ($\text{C}\equiv\text{N}$) to achieve the desired degree of cure (i.e., crosslinking). In some embodiments, the elastomer contains at least 0.1 mole % of nitrile groups, e.g., at least 0.5 or even at least 1 mole % of nitrile groups. In some embodiments, the fluorinated elastomer contains no greater than 5, e.g., no greater than 2 or even no greater than 1.5 mole % of nitrile groups.

[0014] In some embodiments, the nitrile groups are introduced by copolymerizing a nitrile-group containing cure site monomer with the other comonomer, e.g., the TFE, PAVE, and PAAE comonomers. Although not particularly restricted, suitable nitrile-containing cure site monomers include $\text{CF}_2=\text{CFOCF}_2\text{CF}(\text{CF}_3)\text{OCF}_2\text{CF}_2\text{CN}$, $\text{CF}_2=\text{CFOCF}_2(\text{CF}_2)_3\text{CF}_2\text{CN}$, and $\text{CF}_2=\text{CFOCF}_2(\text{CF}_2)_3\text{CF}(\text{CF}_3)\text{CN}$.

[0015] The ammonium hydroxybenzoate compounds of the present disclosure can be used to cure highly fluorinated, nitrile-group containing elastomers. Generally, the ammonium hydroxybenzoate compounds act as catalysts to form triazine crosslinks from the pendant nitrile groups, crosslinking the elastomer to form a cured compound.

[0016] Generally, the ammonium hydroxybenzoate compounds can be blended with the highly fluorinated elastomer and formed into articles such as sheets and O-rings using commonly known equipment and methods. For example, the compounded elastomer composition can be press cured at temperatures of at least 175 °C, e.g., at least 185 °C. In some embodiments, the press curing temperature is no greater than 225 °C, or even no greater than 200 °C. The extent of cure can be determined according to the Cure Rheology Procedure described in the Examples.

[0017] The press cure time is selected to achieve a desired level of cure, which can be indicated by the $\text{Tan } \delta$ at M_H . Generally, adequate cure is indicated by a $\text{Tan } \delta$ at M_H of no greater than 0.5, e.g., no greater than 0.2, or even no greater than 0.1, as determined according to the Cure Rheology Procedure. For most applications, t_{90} (as determined according to the Cure Rheology Procedure) should be less than 20 minutes, for example no greater than 10 minutes. To minimize the risk of scorching, t_{90} should be at least 2 minutes. In some embodiments, longer cure times, e.g., a t_{90} value of at least 4 minutes may be beneficial.

[0018] In some embodiments, the press cured samples may also be post cured. Although not particularly limited, typical post curing temperatures are at least 200 °C, e.g., at least 250 °C and no

greater than 325 °C, e.g., no greater than 300 °C. Post curing times can depend on a variety of factors including the press curing conditions and the post curing temperature. In some embodiments, post curing times are at least 10 hours, e.g., at least 15 hours. In some embodiments, post curing times of no greater than 30 hours, e.g., no greater than 25 hours are desired.

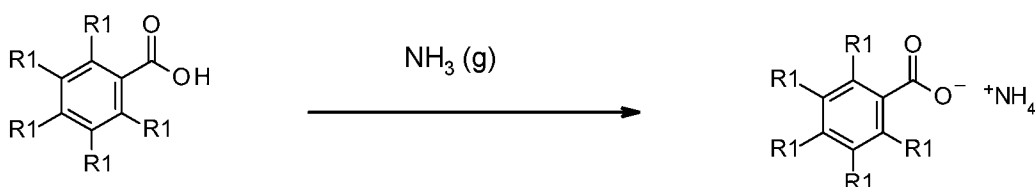
[0019] In some applications, for examples, O-rings and seals, the compression set is a critical property. In some embodiments, the cured compositions of the present disclosure have improved compression set, especially at higher temperatures, e.g., at 250 °C or even 300 °C. In some embodiments, the cured compositions have a compression set of no greater than 40%, e.g., no greater than 35%, or even no greater than 30%, after 70 hours at 250 °C, as measured in accordance with ASTM D 395-03 Method B and ASTM D 1414-94 with an initial deflection of 25 percent. In some embodiments, the cured compositions have a compression set of no greater than 40%, e.g., no greater than 35%, or even no greater than 30%, after 70 hours at 300 °C, as measured in accordance with ASTM D 395-03 Method B and ASTM D 1414-94 with an initial deflection of 25 percent.

[0020] Examples. Materials used in the preparation of the samples are summarized in Table 1.

Table 1: Summary of materials used in the preparation of the examples.

Description	Trade Name and Source
fluorinated onium catalyst (20 wt.% in a perfluoroelastomer)	3M™ Dyneon™ PFE 01CZ, 3M Company
perfluoroelastomer with nitrile cure site groups	3M™ Dyneon™ PFE 131 TZ, 3M Company
benzoic acid (CAS 65-85-0)	Alfa Aesar, 36230
2-hydroxybenzoic acid (CAS 69-72-7)	Alfa Aesar, 30782
4-hydroxybenzoic acid (CAS 99-6-7)	Alfa Aesar, A13700
3,4,5-trihydroxybenzoic acid (CAS 149-91-7)	Alfa Aesar, B24887
4-hydroxy-3-methoxybenzoic acid (CAS 121-34-6)	Oakwood Chemical, 075247

[0021] Generally, ammonium benzoates are commercially available. However, such compounds can also be formed by reacting the corresponding benzoic acid compounds with NH₃ e.g., according to the following reaction.



[0022] The ammonium benzoate compounds used in the present Examples are summarized in Table 2. The compounds were prepared by dissolving the corresponding benzoic acid in a minimum amount of ethanol at room temperature. In a separate flask, an ammonium hydroxide solution (25-30 wt.% ammonium hydroxide) was gently heated to produce ammonia vapor that was then bubbled through the benzoic acid solutions. Ammonia addition was continued until further heating from the exothermic reaction stopped. During the reaction the ammonium benzoates precipitated from solution. Upon reaction

completion, the products were vacuum filtered and rinsed with acetone. Remaining solvent was removed in vacuo with a rotary evaporator. The ammonium benzoates were obtained as white solids and used without further purification.

Table 2: Non-fluorinated onium benzoate curatives

Sample	Ammonium Curative	Hydroxy substitutions	Other substitutions
CE-1	benzoate	none	none
CE-2	4-methyl benzoate	none	alkyl
CE-3	4-methoxy benzoate	none	alkoxy
EX-1	2-hydroxy benzoate	one	none
EX-2	4-hydroxy benzoate	one	none
EX-3	4-hydroxy-3-methoxy benzoate	one	alkoxy
EX-4	3,4,5-trihydroxy benzoate	three	none
EX-5	3,4,5-trihydroxy benzoate	three	none

[0023] Reference Example REF-1 was prepared using a conventional fluorinated onium catalyst. A curable composition was prepared by combining 94 parts by weight of a perfluoroelastomer containing nitrile cure site groups (3M™ DYNEON™ PFE 131 TZ fluoroelastomer from 3M Company) and 7.5 parts by weight of a fluorinated onium catalyst (3M™ DYNEON™ PFE 01CZ catalyst from 3M Company). As this catalyst product consists of 20% by weight of the fluorinated onium catalyst in 80% by weight of a perfluorinated elastomer, the result was 100 parts by weight of the perfluorinated resin and 1.5 parts by weight of the catalyst per 100 parts of the perfluorinated resin (i.e., 1.5 phr).

[0024] Additional samples were prepared from a curable composition containing 100 parts by weight perfluoroelastomer (3M™ DYNEON™ PFE 131 TZ) and 0.5 phr of various non-fluorinated ammonium benzoate curatives. Comparative Examples CE-1, CE-2 and CE-3 were prepared using 0.5 phr of an ammonium benzoate curative that did not include a hydroxy group. Examples EX-1 to EX-4 were prepared using 0.5 phr of various ammonium hydroxybenzoate curatives. These compounds are summarized in Table 2.

[0025] The samples were press cured and the torque as a function of time was recorded according to the following Cure Rheology Procedure. The results are summarized in Table 3.

[0026] Cure Rheology Procedure. Cure rheology tests were carried out using uncured, compounded samples using a rheometer marketed under the trade designation PPA 2000 by Alpha technologies, Akron, OH, in accordance with ASTM D 5289-93a at 188 °C, no pre-heat, 60 minutes elapsed time and a 0.5 degree arc. Both the minimum torque (M_L) and the maximum torque (M_H) were measured in units of inch•pounds and converted to deciNewton•meters (dN•m). If no plateau or maximum torque was obtained, the highest torque attained during the specified period of time was reported as M_H . The time for the torque to reach a value equal to $M_L + 0.1(M_H - M_L)$, ($t'10$); the time for the torque to reach a value equal to $M_L + 0.5(M_H - M_L)$, ($t'50$); and the time for the torque to reach $M_L + 0.9(M_H - M_L)$, ($t'90$) were also measured. The ratios of the viscous torque over the elastic torque were determined at the minimum and maximum torque and are reported as the $\tan \delta$.

[0027] As shown in Table 3, the samples using the non-fluorinated ammonium benzoate and hydroxybenzoate compounds provided similar cure as compared to the conventional fluorinated onium catalyst, as indicated by $\tan \delta$ at M_H values of less than 0.1. However, the t_{90} values for each of the benzoate compounds with no hydroxy substituents were less than 2 minutes, which would result in undesired scorching and processing challenges in some applications.

Table 3: Cure rheology results

Property	REF-1	CE-1	CE-2	CE-3	EX-1	EX-2	EX-3	EX-4
Time (minutes)	30	15	15	15	15	15	15	15
Temperature (°C)	188	188	188	188	188	188	188	188
M_L , min. torque (dN•m)	0.64	2.7	3.0	2.8	2.8	2.7	3.7	1.5
M_H , max. torque (dN•m)	7.7	9.0	8.7	7.8	9.5	9.6	9.2	8.9
t_{10} (minutes to 10% cure)	1.7	0.45	0.42	0.45	0.47	0.51	0.40	1.3
t_{50} (minutes to 50% cure)	3.4	0.71	0.64	0.71	0.78	0.89	0.70	3.2
t_{90} (minutes to 90% cure)	9.3	1.4	1.2	1.5	2.0	2.3	4.1	8.2
$\tan \delta$ at M_H	0.066	0.049	0.057	0.076	0.046	0.044	0.052	0.067
$\tan \delta$ at M_L	1.2	0.61	0.55	0.57	0.57	0.59	0.44	0.081

[0028] The samples were also evaluated according to the following Compression Set Procedure. The results are summarized in Table 4, reported as a percentage.

[0029] Compression Set Procedure. O-rings (214, AMS AS568) were molded and press-cured at 188 °C for 15 minutes, except for REF-1, which was press-cured for 30 minutes. The press-cured O-rings were then post-cured at 250 °C for 16 hours. The post-cured O-rings were subjected to compression set testing for 70 hours at 250 °C or 300 °C in accordance with ASTM D 395-03 Method B and ASTM D 1414-94 with an initial deflection of 25 percent.

Table 4: Compression set results (* 1 of 3 samples cracked during testing)

Property	REF-1	CE-1	CE-2	CE-3	EX-1	EX-2	EX-3	EX-4
Press cure time (minutes)	30	15	15	15	15	15	15	15
Press cure temperature (°C)	188	188	188	188	188	188	188	188
Post cure time (hours)	16	16	16	16	16	16	16	16
Post cure temperature (°C)	250	250	250	250	250	250	250	250
Compression Set (%)								
70 hours at 250 °C	45	21	33	55	20	21	28	48
70 hours at 300 °C	77*	47*	55	90	29	26*	43	64

[0030] As shown by the results in Table 4, the use of the hydroxy-substituted benzoate curatives resulted in substantial improvements in compression set as compared to the fluorinated onium compound, particularly at higher use temperatures.

[0031] Example EX-5 was prepared using the same materials as EX-4 including 0.5 phr of ammonium 3,4,5-trihydroxy benzoate as the curative. Samples were prepared and tested according to the methods described above, except that the samples of EX-5 were press-cured at 188 °C for 30 minutes instead of 15 minutes. The compression set measured after 70 hours at 300 °C was 57%.

[0032] Generally, the ammonium hydroxybenzoate compounds of the present disclosure can be used in the same curable compositions and cured using the same conditions as the traditional fluorinated onium catalysts. Despite being non-fluorinated, the ammonium hydroxybenzoate compounds can provide the same or similar cure performance without introducing low molecular weight fluorinated compounds. In addition, the use of the ammonium hydroxybenzoate compounds can provide significant improvements in the compression set while maintaining higher t₉₀ values as compared to the fluorinated onium compound and onium benzoate compounds that have no hydroxy substituents.

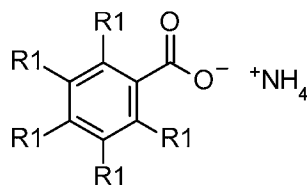
[0033] The Compression Set Procedure and the Cure Rheology Procedure recited in the attached claims refer to the test methods described in the Example portion of this specification.

What is Claimed is:

1. A composition comprising

(i) an uncured highly fluorinated elastomer comprising nitrile groups, wherein at least 80 mole% of the hydrogen atoms of the polymer backbone of the highly fluorinated elastomer have been replaced with fluorine atoms; and

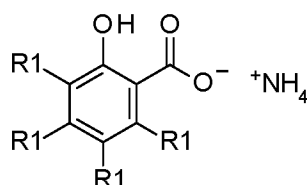
(ii) an ammonium hydroxybenzoate compound according to the formula



wherein: each R1 group is independently selected from the group consisting of H, OH, R and OR, provided that at least one R1 group is OH, and wherein R is an alkyl group, preferably a C₁ to C₄ alkyl group.

2. The composition of claim 1, wherein only one R1 group is OH.

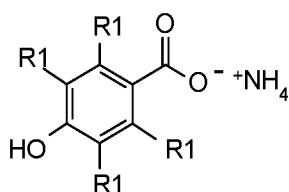
3. The composition of claim 2, wherein the ammonium hydroxybenzoate compound is



wherein each R1 group is independently selected from the group consisting of H, R and OR.

4. The composition of claim 3, wherein each R1 group is H.

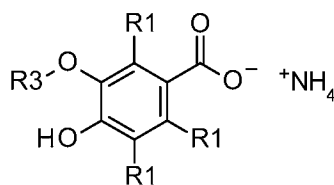
5. The composition of claim 2, wherein the ammonium hydroxybenzoate compound is



wherein each R1 group is independently selected from the group consisting of H, R and OR.

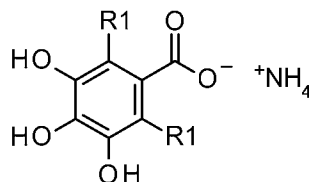
6. The composition of claim 5, wherein each R1 group is H.

7. The composition of claim 5, wherein the ammonium hydroxybenzoate compound is



wherein each R1 group is H, and R3 is a C1 to C4 alkyl group.

8. The composition of claim 1, wherein the ammonium hydroxybenzoate compound is



wherein each R1 group is H.

9. The composition of any one of the preceding claims, wherein at least 95 mole % of the hydrogen atoms of the polymer backbone of the uncured highly fluorinated elastomer have been replaced with fluorine atoms.

10. The composition of any one of the preceding claims, wherein the uncured highly fluorinated elastomer comprises repeating units derived from a perfluorinated monomer comprising a nitrile group, tetrafluoroethylene (TFE), and at least one comonomer selected from the group consisting of a perfluoroalkyl vinyl ether (PAVE) and a perfluoroalkyl allyl ether (PAAE).

11. The composition of any one of the preceding claims, wherein the uncured highly fluorinated elastomer comprises at least 1 mole % and no greater than 5 mole % of nitrile groups.

12. A cured elastomer prepared from the composition according to any one of claims 1 to 11, wherein the uncured highly fluorinated is cured by the ammonium hydroxybenzoate compound to form triazine crosslinks.

13. The cured elastomer of claim 12, having a compression set of no greater than 40% after 70 hours at 300 °C, as measured according to the Compression Set Procedure.

14. The cured elastomer of claim 12 or 13, wherein the cured elastomer has a Tan δ at M_H of less than 0.1 as measured according to the Cure Rheology Procedure or wherein the composition has t'_{90} value of at least 2 minutes and no greater than 20 minutes, as measured according to the Cure Rheology Procedure.

15. An article comprising the cured elastomer according to any one of claims 11 to 14.

INTERNATIONAL SEARCH REPORT

International application No

PCT/IB2022/053212

A. CLASSIFICATION OF SUBJECT MATTER**INV. C08K5/19****ADD.**

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

C08K

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

EPO-Internal, WPI Data**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	DATABASE WPI Week 202001 Thomson Scientific, London, GB; AN 2020-129822 XP002806952, -& WO 2020/031673 A1 (DAIKIN IND LTD) 13 February 2020 (2020-02-13) abstract	1-15
A,P	-& EP 3 835 352 A1 (DAIKIN IND LTD [JP]) 16 June 2021 (2021-06-16) paragraph [0068] - paragraphs [0069], [0077] examples 1,2; table 1 claims 1-8	1-15
A	US 5 565 512 A (SAITO SATORU [JP] ET AL) 15 October 1996 (1996-10-15) examples 10,14 claims	1-15



Further documents are listed in the continuation of Box C.



See patent family annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/IB2022/053212

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
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