Oversættelse af europæisk patentskrift

Patent- og Varemærkestyrelsen

Int.Cl.: A 61 K 6/02 (2006.01)  C 04 B 41/00 (2006.01)  C 04 B 41/82 (2006.01)

Oversættelsen bekendtgjort den: 2017-07-17

Dato for Den Europæiske Patentmyndigheds bekendtgørelse om meddelelse af patentet: 2017-03-22

Europæisk ansøgning nr.: 13823937.1

Europæisk indleveringsdag: 2013-12-23

Den europæiske ansøgnings publiceringsdag: 2015-10-28

International ansøgning nr.: EP2013003938

International publikationsnr.: WO2014095089

Prioritet: 2012-12-22 DE 102012025342

Designerede stater: AL AT BE BG CH CY CZ DE DK EE ES FI FR GB GR HR HU IE IS IT LI LT LU LV MC MK MT NL NO PL PT RO RS SE SI SK SM TR

Patenthaver: METOXIT AG, Emdwiesenstrasse 6, 8240 Thayngen, Schweiz

Opfinder: KAMPFER, Konrad, Zieglerweg 2b, CH-8240 Thayngen, Schweiz
ELMAZI, Denis, Breiltesteg 26, CH-8200 Schaffhausen, Schweiz

Fuldmaægig i Danmark: Chas. Hude A/S, H.C. Andersen Boulevard 33, 1780 København V, Danmark

Benævnelse: FREMGANGSMÅDE TIL AT FORØGE STYRKEN AF KERAMIK

Fremdragne publikationer:
JP-A- S6 456 386
Description

[0001] The invention relates to a method for increasing the strength of ceramics, in particular oxide ceramics, in particular for technical, medical and dental applications.

[0002] In the state of the art, there are various possibilities for achieving an increase in the strength of ceramics. In dental medicine, not only are the aesthetics of great importance but the mechanical properties of ceramics also play a key role. In other medical and technical applications, the homogeneity and strength of the ceramic is an important criterion.


[0004] It is disadvantageous in the state of the art that the maximum theoretically possible strength of ceramics is not fully utilized.

[0005] An object of the present invention is therefore to provide a method for increasing the strength of ceramics in which the strength of the ceramics is increased in comparison with the state of the art. This result can also particularly advantageously be achieved with lower energy expenditure.

[0006] An object of the present invention is consequently to indicate a method for increasing the strength of ceramics in which an increase in the flexural strength and reliability and thus an improvement in the utilizable strength arise.

[0007] This object is achieved by a method for increasing the strength of ceramics according to claim 1.

[0008] This object is furthermore achieved by a ceramic according to claim 12.

[0009] Further advantageous embodiments of the present invention are indicated in the dependent claims.

[0010] According to an aspect of the invention, a method is provided for increasing the strength of ceramics, in particular oxide ceramics, preferably made of zirconium oxide, aluminium oxide or mixtures thereof, particularly preferably dental ceramics, comprising the steps of

  - provision of a pre-sintered ceramic and
treatment of the pre-sintered ceramic with a solution based on carboxylic
acid, preferably citric acid, wherein the concentration of the carboxylic
acid in the solution is between 20 and 65 wt.-%, preferably between 40
and 55 wt.-% and is particularly preferably 50 wt.-%.

[0011] A pre-sintered ceramic is a green compact or a white body, i.e. a
ceramic shaped body which has already been thermally treated at least once,
but has not yet been fully sintered. The starting material for the green compact
may preferably also already be treated with a solution based on carboxylic acid,
preferably citric acid, and only therefrom may the shaped body be produced, in
particular pressed.

[0012] The treatment of the pre-sintered ceramic with a solution based on
carboxylic acid preferably causes an infiltration of the pre-sintered ceramic with
this carboxylic acid, preferably citric acid. The pre-sintered ceramic treated in
this way has the property that it can be sintered during the full sintering process
to give a more stable finally sintered ceramic body with increased strength.

[0013] The method preferably additionally comprises the step of staining the
porous pre-sintered ceramics with the solution based on carboxylic acid,
preferably citric acid, wherein the solution preferably also comprises
chromophoric components.

[0014] The staining of the ceramic has only a slight influence on the developing
strength of the ceramic. Conversely, the developing strength of the ceramic
does not influence the staining process either.

[0015] In a particularly preferred embodiment of the invention, the method
comprises the step of final sintering (full sintering, dense sintering) of the pre-
sintered ceramic.

[0016] The full sintering process preferably passes through several steps,
during which the porosity and volume of the green compact are clearly reduced.
In the first step at approx. 1000°C to 1200°C, only a precompacting of the green
compact takes place, whereas in the second step at 1200 to 1400°C the open
porosity is already clearly reduced. The strength of the sintered bodies then
develops in the third step at approx. 1400°C to 1600°C, upon completion of
which the ceramic bodies are entirely fully sintered, no longer have pores and obtain their strength.

[0017] Surprisingly, it was established in a method described according to the invention that the temperature in the third step could be lowered from 1450°C to only 1300°C and the same degree of dense sintering could be achieved with increased strength. It is thus preferably possible to dispense with the third sintering step since the ceramic body is already fully sintered with the second sintering step at approx. 1300°C.

[0018] In addition, it was surprisingly found that the strength of the fully sintered ceramic could be considerably increased by the treatment with the carboxylic acid.

[0019] At the same time, it is also possible to guarantee an increase in the strength of the ceramic in addition to the staining of the ceramic. The staining of the ceramic has only a slight influence on the developing strength of the pre-sintered ceramic and vice versa.

[0020] In a further particularly preferred embodiment of the invention, the ceramics are preferably ceramics for medical applications, in particular dental ceramics or technical ceramics.

[0021] Technical ceramics are preferably ceramics for bearing and sealing technology, for sliding rings, for sealing discs, for wire drawing, for tube forming, for hard coverings, for thread guiding, for thread shaping, for the production of yarns, for cutting utensils (blades) and for electrical engineering/electronics.

[0022] The term ceramic also encompasses the objects themselves formed and fired from ceramics, which are used as components, articles of daily use and decorative items or tools, in addition to the materials which are used for the production of ceramic products and the processing thereof to give the actual ceramic (clay-based ceramic, technical ceramic, composite ceramic).

[0023] In a precursor to the sintered body, a green compact is pre-sintered to form a ceramic body referred to as a white body. A green compact is a body which is compacted by a thermal process before its intended use. In the production of ceramics, the green compact is generally produced by casting, plastic forming or pressing. Complex components can be manufactured accurately shaped by casting; components can be produced inexpensively by
plastic forming such as, for example, extrusion. Large numbers of items can be produced inexpensively by pressing. During pre-sintering of the green compacts to form the white body, a temperature of from 600°C to 1100°C is preferably chosen.

[0024] In addition to the carboxylic acid, the solution preferably contains water and/or stabilizing alcohols. The pre-sintered ceramic can thus be treated in a targeted manner.

[0025] Weak acids dissociate only partially in water; strong acids, by contrast, dissociate completely in water. The acidity constant or the pKₐ value is therefore a measure of the strength of an acid. The smaller the pKₐ value, the greater is the acidity. The pKₐ value is the negative common logarithm of the pH value. The carboxylic acid preferably has a pH of 0.1 - 2.5, preferably of from 0.4 to 1.2 and particularly preferably of 0.8.

[0026] A good distribution of the components in the solution is to be achieved by the chromophoric components contained in the solution. A colour application with uniform coverage can thus be accomplished when the ceramic is stained.

[0027] The chromophoric components are particularly preferably dissolved in the carboxylic acid.

[0028] A targeted distribution of the chromophoric components in the carboxylic acid is thus possible. The prepared carboxylic acid enriched with the colouring components can then be mixed in a solution according to requirements.

[0029] The method preferably has the step of processing of the pre-sintered ceramic before the treatment with a solution to form a framework ceramic.

[0030] Framework ceramics are crowns, bridges and also pontics for dental technology. The framework ceramics are carved out of the pre-sintered ceramic blank before the treatment with the solution. The carving out is preferably a turning, milling, drilling, grinding, polishing and/or sandblasting process which gives the blank its corresponding shape.

[0031] It is thus possible to treat the fully milled framework ceramic with the solution.

[0032] The method particularly preferably has the step of staining the ceramic by immersion in the solution.
[0033] The process of immersing the ceramic in the solution brings about an infiltration process in the ceramic. The pre-sintered ceramic preferably has a porosity which allows the solution to partially or completely penetrate/infiltrate into the available pores of the ceramic body until a saturation of the ceramic, which meets requirements, is reached.

[0034] The immersion process preferably lasts between 3 min and up to 14 h, depending on the size or wall thickness of the ceramic, until the infiltration process is completed.

[0035] It is particularly advantageous that the colour intensity when staining with corresponding components in the solution is dependent on the concentration of the solution alone and not, as in the state of the art, on the immersion time.

[0036] It is also particularly advantageous that the solution can partially or completely infiltrate into the porous ceramic with dimensions above 10 mm thickness or corresponding wall thicknesses.

[0037] It is furthermore advantageous that the infiltration solution also remains in the porous ceramic upon complete saturation and does not run out again.

[0038] The method particularly preferably has the step of pressurized application of the solution onto the ceramic during the immersion process.

[0039] Through the pressurized application of the solution onto the ceramic during immersion in the solution, it is possible to introduce or push the solution into the ceramic more quickly, with the result that the infiltration process can be accelerated. By means of the pressurized application, an infiltration, preferably over the course of from 0.5 min to 5 h, is possible depending on the size of the ceramics, which results in a shortening of the infiltration process.

[0040] The method particularly preferably has the step of individual staining of the framework ceramics by means of a device for colour application.

[0041] The device for colour application is preferably a brush, a pen or a spraying device. Targeted staining of the pre-sintered ceramic is thus possible. A variable colour application onto the ceramic can thus particularly preferably also be accomplished.

[0042] The method particularly preferably facilitates the step of treatment of the pre-sintered ceramics with at least one further solution which is different from the first solution.
[0043] It is thereby possible to introduce a further second colouring component into the ceramic building on the first layer.

[0044] The ceramic is preferably only infiltrated until a certain degree of saturation is reached, i.e. free pores are still available. The ceramic is then immersed in at least one further solution until a partial or final saturation of the ceramic, which meets requirements, is reached, i.e. no free pores are available.

[0045] This effect leads to a layered intensification of the colouring and an additional increase in strength when, for example, citric acid is used as first carboxylic acid.

[0046] The chromophoric components are particularly preferably metal ions or metal complexes contained in the solution which comprise the salts Fe, Cr, Co, Mn, Cu, Pr, Er, Nd or other staining oxides of elements from the group of rare earths, preferably ammonium ferric citrate.

[0047] In tests, it has been shown that the ceramics can usefully be stained with oxides or salts of Fe, Cr, Co, Mn, Cu, Pr, Er, Nd or other elements from the group of rare earths that are suitable for staining.

[0048] Ammonium ferric citrate is preferably used for the staining and good results can be achieved therewith. Ammonium ferric citrate is preferably present in the solution in a quantity of between 1.5 and 5.0 wt.-%, particularly preferably of 2.5 wt.-%.

[0049] The metal ions are particularly preferably present in the solution in a quantity of 0.05 wt.-% and metal complexes in a quantity of 40 wt.-%.

[0050] It is thereby possible to accomplish a homogeneous or layered staining of ceramic components, even with a considerably greater component height or thickness of 10 mm.

[0051] In tests, it has been shown that good staining results can be achieved with these values for metal ions and metal complexes.

[0052] The carboxylic acid is particularly preferably an acetic acid, butyric acid, salicylic acid, aconitic acid or citric acid, among others. It is also possible to use combinations and mixtures of these acids.

[0053] Furthermore, the carboxylic acid is particularly preferably an oxalic acid, fumaric acid, benzoic acid, nicotinic acid, abietic acid, oleic acid, succinic acid, maleic acid or a pyrrolidine-II-carboxylic acid as well as mixtures thereof.
[0054] Similar increases in strength of the individual ceramics can thereby be achieved with different carboxylic acids.

[0055] The provision of different carboxylic acids with the addition of chromophoric components furthermore leads to the ceramics being formed differently in terms of colour.

[0056] The concentration of the carboxylic acid in the solution is between 20 and 65 wt.-%, preferably between 40 and 55 wt.-% and is particularly preferably 50 wt.-%.

[0057] The best results for the increase in strength and the staining using the named carboxylic acids could be achieved at a concentration of between 20 and 65 wt.-%. Using the example of citric acid as carboxylic acid, the highest strength and the most intensive colouring could be realized at a value of approx. 50 wt.-%.

[0058] The pre-sintered ceramics are particularly preferably oxide-ceramic materials with open pores, preferably 3Y-TZP-A, ATZ, Al2O3 in opaque or translucent form, dispersion ceramics or glass-phase bonded ceramics.

[0059] Oxide-ceramic materials are one-component systems or multicomponent systems.

[0060] One-component systems preferably consist of aluminium oxide, magnesium oxide, zirconium oxide or titanium oxide.

[0061] Multicomponent systems preferably consist of aluminium titanate (mixed form of aluminium oxide and titanium oxide), mullite (mixed form of aluminium oxide and silicon oxide), lead zirconate titanate (piezoelectric ceramic), or of dispersion ceramics such as Zirconia Toughened Alumina (ZTA) - Al2O3/ZrO2 or Alumina Toughened Zirconia (ATZ).

[0062] Further preferred ceramics contain glass phases by means of which the sintering temperature is lowered. At the same time, the strength of these ceramics is also reduced.

[0063] On the other hand, a ceramic with an average or high content of zirconium oxide is characterized by increased or high strength. (Examples: ZTA, Zirconia Toughened Alumina, 80% Al2O3, 20% ZrO2, strength up to 1300 MPa; ATZ, Alumina Toughened Zirconia, 80% ZrO2, 20% Al2O3, strength up to 2000 MPa.)
The porosity of the ceramics is preferably approximately 10 - 50 vol.-%, particularly preferably 45 vol.-%. In tests, good results could be achieved at a porosity of 45 vol.-%.

The pre-sintered ceramics are particularly preferably translucent or opaque ceramics with open pores.

Because of their porosity, ceramics with open pores have the ability to take up a solution based on carboxylic acid by absorbing it. This absorption effect lasts until the ceramic is saturated.

Translucent ceramics are those which exhibit light transmission.

The reciprocal property of translucency is opacity. Thus, if a substance has a high translucency, it has a low opacity, and vice versa.

Different light transmittance values can thus be achieved with translucent or opaque ceramics in ceramics production.

Ceramics are particularly preferably stained homogeneously throughout, in a layered manner or with a colour gradient.

The at least partial immersion of the ceramics in different, colouring infiltration solutions facilitates a multistep, layered colouring of the pre-sintered ceramics.

Staining without colour boundaries develops during the immersion process in a colouring infiltration solution.

A colour gradient is achieved by the repeated, successive immersion of the ceramics in different colouring infiltration solutions.

According to a further aspect of the invention, a pre-sintered ceramic is provided which was infiltrated with a solution based on carboxylic acid, in particular citric acid, after the pre-sintering, wherein the concentration of the carboxylic acid in the solution is between 20 and 65 wt.-%, preferably between 40 and 55 wt.-% and is particularly preferably 50 wt.-%.

A pre-sintered ceramic which was treated with a solution based on carboxylic acid is thus provided. The pre-sintered ceramic preferably has a porosity which allows the solution to partially or completely penetrate/infiltrate into the available pores of the ceramic body such that an infiltration process can take place.
[0076] A ceramic pre-sintered in this way only exhibits a small increase in strength, with or without staining, compared with a pre-sintered ceramic known from the state of the art.

[0077] The strength of a ceramic treated with carboxylic acid and then densely sintered can, on the contrary, be more than doubled after the dense sintering compared with ceramics not treated according to the method.

[0078] Further advantages and details of the invention are explained with reference to the embodiment examples represented in the figures.

[0079] There are shown in detail in the figures:

Figure 1 a diagram of the characteristic flexural strength $\sigma_0$ of three ceramic samples A, B, C made of zirconium oxide with an aluminium oxide content of 0.05 wt.-%,

Figure 2 a Weibull analysis of a non-infiltrated sample with an aluminium oxide content of 0.05 wt.-%,

Figure 3 a Weibull analysis of an infiltrated sample without staining with an aluminium oxide content of 0.05 wt.-%,

Figure 4 a Weibull analysis of an infiltrated sample with staining with an aluminium oxide content of 0.05 wt.-%,

Figure 5 a comparison of the densities of infiltrated samples vs. non-infiltrated ceramic samples from Figure 1,

Figure 6 strengths of untreated ceramics as well as of infiltrated or infiltrated and stained translucent ceramics from Figure 1 and

Figure 7 Weibull moduli of non-infiltrated, infiltrated and infiltrated/stained, translucent zirconium oxide ceramics from Figure 1.
[0080] Figure 1 represents a diagram of the characteristic flexural strength $\sigma_0$ of three ceramic samples A, B, C made of zirconium oxide with an aluminium oxide content of 0.05 wt.-%.

[0081] The highly translucent zirconium oxide blanks preferably used today in dental medicine or in the technical field differ by a reduced aluminium oxide proportion of from 0.05 to 0.1 per cent by weight from opaque 3-Y-TZP-A with 0.25% per cent by weight Al$_2$O$_3$. A typical lower strength of approx. 800 - 1000 MPa of translucent ZrO$_2$ contrasts with typical flexural strengths of opaque ZrO2 of approx. 1200 MPa.

[0082] The translucent starting materials examined here (samples with reference REF) are identified by the aluminium oxide proportion 0.05 wt.-% (sample REF 0.05). The strengths of the starting materials reach 1052 MPa at Weibull moduli $m_{cor}$ of 8.56. The confidence level is in each case 90%.

[0083] The translucent materials which were subjected to an infiltration bear the reference RB 0.05 (0.05% Al$_2$O$_3$).

[0084] The influence of the RB infiltration of a porous pre-sintered ceramic on the final sintering strength is examined. By comparison of static biaxial strength tests (ball on 3 balls, similar to ISO 6872) of samples with the reference REF, an increase in strength to 2532 MPa is evident through RB infiltration.

[0085] In each case 30 test specimens from standard discs from Metoxit AG were used for the tests (Z-CAD HD 99-14 HTL discs from the identical zirconium oxide raw material), wherein REF denotes the non-infiltrated test specimens of standard quality and RB denotes the infiltrated samples.

[0086] The test specimens for the strength determination were cut dry from the pre-sintered discs and separated to form small plates (14.0 x 14.0 x 1.5 mm). The evaluation is carried out in accordance with ISO 6872.

[0087] In conclusion, it should be noted that the infiltration method RB considerably increases the strength in the static flexural strength test.

[0088] The tests have furthermore shown that the infiltration does not adversely affect the density.

[0089] Figure 2 represents a Weibull analysis of a non-infiltrated sample with an aluminium oxide content of 0.05 wt.-%.
[0090] The strength in the biaxial B3B method is 1052 MPa and the Weibull modulus $m = 8.56$.

[0091] The Weibull distribution per se is a continuous probability distribution over the quantity of positive real numbers, which is used, for example, to describe lifetimes and failure rates of e.g. (brittle) materials (for instance in quality assurance).

[0092] The Weibull distribution can be used to describe rising, constant and falling failure rates of technical systems. In practice, the Weibull distribution is the most frequently used lifetime distribution alongside the exponential distribution, which is a special case of the more general Weibull distribution. A high Weibull modulus is sought.

[0093] Figure 3 represents a Weibull analysis of an infiltrated sample without staining with an aluminium oxide content of 0.05 wt.-%.

[0094] The strength in the biaxial B3B method is 2532 MPa and the Weibull modulus $m = 15.37$.

[0095] Figure 4 represents a Weibull analysis of an infiltrated sample with staining with an aluminium oxide content of 0.05 wt.-%.

[0096] The strength in the biaxial B3B method is 2247 MPa and the Weibull modulus $m = 11.79$.

[0097] Figure 5 shows a comparison of the densities of infiltrated samples vs. non-infiltrated ceramic samples from Figure 1.

[0098] All the samples A, B, C have the same density of 6.09 g/cm$^3$. The tests have shown that neither the infiltration nor the staining adversely affects the density.

[0099] Figure 6 represents strengths of untreated ceramics as well as of infiltrated or infiltrated and stained translucent ceramics from Figure 1.

[0100] Here, the strengths of untreated ceramics with the reference REF 0.05 as well as the strengths of an infiltrated (ref. RB) or infiltrated and stained (ref. RB + colour) translucent ceramic are shown.

[0101] Figure 7 represents the Weibull moduli of non-infiltrated, infiltrated and infiltrated/stained, translucent zirconium oxide ceramics from Figure 1.

[0102] The Weibull modulus is a measure of the homogeneity and thus the reliability in respect of the strength of ceramics. A high strength value at the
same time as a high Weibull modulus is therefore sought. The Weibull moduli of the infiltrated samples are clearly higher than those of the non-infiltrated samples, with the consequence that the reliability of the infiltrated ceramics compared with the non-infiltrated ceramics is increased to an extraordinary extent.

[0103] It is thus evident that by using concentrated strong carboxylic acids a method is provided with which ceramic components in the pre-sintered state can be treated in such a way that the mechanical strengths and reliabilities in the densely sintered state can thereby be massively increased. The optional staining of the pre-sintered ceramics in addition also hardly influences the increase in strength of the fully sintered ceramics.

[0104] Tests furthermore show that infiltrated ceramics, in particular mixed ceramics made of zirconium oxide and aluminium oxide reach the theoretical density and thus final dense sintering at a lower sintering temperature than hitherto generally known.

[0105] Furthermore, a clear increase in strength is also established in the case of infiltrated high-purity aluminium oxide ceramics.
Patentkrav

1. Fremgangsmåde til at forøge styrken af keramik, især oxidkeramik, der fortrinsvis er fremstillet af zirconiumoxid, aluminiumoxid eller blandinger deraf, hvilken fremgangsmåde omfatter trinene

- at tilvejebringe en for-sintret keramik og
- at behandle den for-sintrede keramik med en opløsning, der er baseret på carboxylsyre, fortrinsvis citronsyre, hvor koncentrationen af carboxylsyren i opløsningen er mellem 20 og 65 vægt-%, fortrinsvis mellem 40 og 55 vægt-% og især fortrinsvis 50 vægt-%.

2. Fremgangsmåde til at forøge styrken af keramik ifølge krav 1, hvilken fremgangsmåde yderligere omfatter trinnet
- slut-sintring af den for-sintrede keramik, der er behandlet med opløsningen, som er baseret på carboxylsyre.

3. Fremgangsmåde til at forøge styrken af keramik ifølge et af de foregående krav, hvor keramikken er tandkeramik eller teknisk keramik.

4. Fremgangsmåde til at forøge styrken af keramik ifølge et af de foregående krav, hvilken fremgangsmåde yderligere omfatter trinnet
- at behandle den for-sintrede keramik før behandling med en opløsning for at danne en skeletkeramik.

5. Fremgangsmåde til at forøge styrken af keramik ifølge et af de foregående krav, hvilken fremgangsmåde yderligere omfatter trinnet
- at behandle keramikken ved at nedsænke den i opløsningen.

6. Fremgangsmåden til at forøge styrken af keramik ifølge krav 5, hvilken fremgangsmåde yderligere omfatter trinet
- at trykpåføre opløsningen på keramikken under nedsænkningsprocessen.
7. Fremgangsmåde til at forøge styrken af keramik ifølge et af de foregående krav, hvilken fremgangsmåde yderligere omfatter trinnet
- at behandle den for-sintrede keramik med mindst en yderligere opløsning, som er forskellig fra den første opløsning.

8. Fremgangsmåde til at forøge styrken af keramik ifølge et af de foregående krav, hvor carboxylsyren er en eddikesyre, smørssyre, salicylsyre, aconitinsyre eller citronssyre.


10. Fremgangsmåde til at forøge styrken af keramik ifølge et af de foregående krav, hvor kromofore komponenter er indeholdt i opløsningen.

11. Fremgangsmåde til at forøge styrken af keramik ifølge et af de foregående krav, hvilken fremgangsmåde yderligere omfatter trinnet
- at indføre kromofore komponenter i opløst form i keramikken ved nedsænkning eller infiltrering med eller uden påføring af tryk.

12. For-sintret keramik, der blev infiltreret med en opløsning, der er baseret på carboxylsyre, især citronssyre, efter for-sintringen, hvor koncentrationen af carboxylsyren i opløsningen er på mellem 20 og 65 vægt-%, fortrinsvis mellem 40 og 55 vægt-% og er især fortrinsvis 50 vægt-%.
Figure 1

- **A**: Ref 0.05
- **B**: RB 0.05
- **C**: RB 0.05 + colour

The diagram illustrates the characteristic flexural strength in MPa for different sample types.
Fig. 2

Fig. 3
Fig. 4

Fig. 5
Figure 6
Figure 7

Diagram showing:
- Sample type along the x-axis.
- Weibull ln(ln(1/(1-P))) along the y-axis.
- Samples labeled A, B, and C.

Legend:
- A: Ref 0.05
- B: RB 0.05
- C: RB 0.05 + colour