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(72) Inventeurs/Inventors:
ANTON, OCTAVIAN, BE;
WU, XIAO, BE

(73) Propriétaire/Owner:
PROMAT INTERNATIONAL N.V., BE

(74) Agent: OGILVY RENAULT LLP/S.E.N.C.R.L.,S.R.L.

(54) Titre : MATERIAU IGNIFUGE
(54) Title: FIRE-PROTECTION MATERIAL

(57) Abrégé/Abstract:
The fire-protection material for constructions made of concrete and prestressed concrete, especially for tunnels, in the form of prefabricated plates or sprayed-on and cured coatings is prepared from hydraulically curing compositions containing aluminous cement, optionally in admixture with Portland cement, fillers and, if desired, fibers, curing accelerators, curing delayers, plasticizing agents and foaming agents, wherein the cured material contains less than 5% by weight of ettringite and wherein the composition contains from 50 to 200 weight parts of aluminous cement and from 10 to 250 weight parts of xonotlite in the uncured composition.

Abstract

The fire-protection material for constructions rnade of concrete and prestressed concrete, especially for tunnels, in the form of prefabricated plates or sprayed-on and cured coatings is prepared from hydraulically curing compositions containing aluminous cement, optionally in admixture with Portland cement, fillers and, if desired, fibers, curing accelerators, curing delayers, plasticizing agents and foaming agents, wherein the cured material contains less than 5% by weight of ettringite and wherein the composition contains from 50 to 200 weight parts of aluminous cement and from 10 to 250 weight parts of xonotlite in the uncured composition.

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Fire-Protection Material

The present invention relates to a fire-protection material, i.e., a material having good fire-protection properties for constructions made of concrete and prestressed concrete, especially for tunnels, in the form of prefabricated plates or sprayed-on and cured coatings prepared from hydraulically curing compositions containing aluminous cement, optionally in admixture with Portland cement, fillers and, if desired, fibers, curing accelerators, curing delayers, plasticizing agents and foaming agents.

A material having good fire-protection properties is the subject of DE C 195 17 267, said material being in the form of prefabricated plates or of a coating to be applied later to construction parts to be protected and consisting of a binder, synthetic xonotlite and at least 5% by weight of ettringite and/or metavariscite. This material has proven very useful, but is not capable of satisfying the higher demands which have been desired and in part already required in the meantime, especially for tunnels. Thus, it is required that, in the case of a fire, no irreparable damage must be caused by the loss of more than 50% of the original strength. The Netherlands require for immersed tunnels that the surface of the concrete core reaches a maximum of 380 °C and the maximum temperature at a distance of 25 mm from the surface of the concrete core reaches only 250 °C. For drilled tunnels, this maximum surface temperature must not exceed 200 to 250 °C; cf. Both et al., TNO Centre for Fire Research, and Tan et al., Minestry of Public Works, The Netherlands. After the fire accident in the Mont Blanc tunnel, the desires for the fire-protection properties for tunnels are further increased.

The Dutch requirements for tunnels are based on the assumption that the combustion energy of a tank truck which had an accident results in a local heating which can be survived by the concrete core of the tunnel wall in a substantially

undamaged condition. Thus, the test of this requirement is to show that a flat or bent plate which is mechanically attached to the surface of the concrete does not drop down; especially sprayed-on coatings tend to lose the adhesion and to detach. The test conditions are based on two hours, wherein the surface temperature of the concrete core must not exceed 200 °C for drilled tunnels and 380 °C for immersed tunnels, the thickness of the concrete being equal to or greater than 150 mm. The material for fire protection must withstand the heat shock, be resistant to abrasion and insensitive towards freeze/thaw cycles. The mechanical strength of this material in a three-point bending test should be as high as possible at 20 °C. Preferably, it should be at least 7 MPa. The material should be resistant to chemical salts. Finally, it should be free of quartz for reasons of environmental protection and public health. The density of the material should be about 900 kg/m^3.

Previously known materials originally developed only for buildings and having good fire-protecting properties are those according to DE C 195 17 267, or the Promatect* H plates manufactured by the Promat company, which are also employed in tunnel construction. These are autoclaved, fiber-reinforced light-weight construction plates on the basis of calcium silicates. They are prepared from Portland cement, silica, expanded pearlites, calcium hydroxide, fibers and other additives. Although employed for tunnel construction, they still fail to meet all the desires and requirements of fire protection for tunnels. In particular, these are the problems of delamination, restricted thickness and possible repair.

Other products of the prior art, which have in part also proven useful, also fail to meet the requirements of tunnel construction. US 4,544,409 describes a material made of cements and trisodium phosphate hydrate. These products melt at relatively low temperatures and are therefore unsuitable for tunnels.

EP 0 769 482 describes a sprayable cement mortar with gypsum and calcium aluminate. This material is not capable either of meeting the requirements of tunnel construction. The same holds for the commercially available plates of the Kurosaki company which, according to analyses, consist of wollastonite, mullite,

* trade-mark

pearlites, glass fibers and synthetic fibers and are bonded with aluminous cement. They have a density of 1050 kg/m^3, but only a bending strength of 4 MPa.

EP 1 001 000, corresponding to WO 00/27948, describes a material which is supposed to be suitable also for tunnels and which contains a component which is volatile at high temperatures due to saw dust being admixed. In the meantime, this material has been placed on the market by the company Thermal Ceramics under the designation Fire Barrier* 135. This material contains kaolin, which is not only expensive, but also shrinks upon strong heating to such an extent that the product becomes cracked. Further, the coating thickness and the adhesive strength are problematic.

Thus, it has been the object of the invention to provide a fire-protection material for constructions of concrete and prestressed concrete which meets the above mentioned enhanced desires and requirements for the fire protection of tunnel constructions and does not cause any health hazards in the case of a fire.

This object is achieved by a material which is prepared from a hydraulically curing composition containing aluminous cement, optionally in admixture with Portland cement, fillers and, if desired, fibers, curing accelerators, curing delayers, plasticizing agents and foaming agents, wherein the cured material contains less than 5% by weight of ettringite, characterized in that the composition contains from 50 to 200 weight parts of aluminous cement and from 10 to 250 weight parts of xonotlite in the uncured state. Preferably, the mixture is prepared from as many or twice as many weight parts of hydraulic binder as there are weight parts of xonotlite.

In the uncured state, the composition may contain Portland cement as an additional hydraulic binder and up to 50% by weight of fillers, optionally fibers, curing accelerators, curing delayers, plasticizing agents and foaming agents. In the cured state, it always contains less than 5% by weight of ettringite.

Preferably employed fillers include wollastonite and/or aluminum hydroxide, but optionally also tobermorite, which may be added in the form of needles or

* trade-mark

approximately spherical parts. As fillers, pearlites and/or vermiculites may also be added, preferably in an already expanded form. However, it is altogether possible to add these fillers entirely or partly in an unexpanded form. Further fillers may be expanded clays, expanded glass spheres or chamotte meal.

Further, fibers may be added to facilitate the preparation process and to reinforce the finished material. Suitable fibers include, for example, glass fibers, MMMF (man-made mineral fibers), cellulose fibers, organic fibers, such as PVA or PP.

Usual curing accelerators, curing delayers, plasticizing agents and foaming agents may be added, especially to facilitate the preparation process. These additives include calcium hydroxide, aqueous sodium hydroxide, sodium carbonate, calcium carbonate, lithium carbonate, borax, citric acid, aluminum hydroxide. Calcium carbonate is preferred; it acts as both a curing accelerator and as a suitable filler.

In the cured state, the material should contain virtually no or only a little ettringite. At any rate, the ettringite content should be always less than 5% by weight. While ettringite is a very important component essential to the invention in the material according to DE C 195 17 267, it is just the larger amounts of ettringite which result in clearly deteriorated properties at the high temperatures which may occur in a tunnel fire.

The preparation of the material in the form of prefabricated plates is preferably effected by casting or filter-pressing, but the Hatschek process or the flow-on process may also be applied. A usual method for the preparation of constructional parts of fibrous cement is the Hatschek process. In this process, a composition consisting of a cement-bonded matrix with inert and reactive fillers as well as of fibers is prepared with a significant excess of water and dehydrated through one or more cylinder molds. The non-woven fabric produced thereby is applied to a transport device, further dehydrated in a vacuum and wound onto a rotating cylinder, the so-called format roller, until the desired thickness of the constructional part has been achieved. The maximum thickness will then be from 25 to 27 mm. For example, the above mentioned commercial product Promatect H is prepared by the Hatschek process.

The amounts of aluminous cement and xonotlite employed according to the invention can be varied within the limits stated, but it is preferred for the composition to contain as many or twice as many weight parts of hydraulic binder as it contains weight parts of xonotlite.

By selecting the kind of fillers, the density of the material in the cured state can be varied within a range of between 0.7 and 1.3 g/cm^3, a density of about 0.9 g/cm^3 being preferred.

The cured material according to the invention has the property of being dehydrated in a stepwise manner predominantly within a temperature range of between 70 and 450 °C and thus is capable to absorb heat step by step and to reduce the increase of temperature in the region between the surface and the substrate to be protected. These properties can be enhanced by endothermic fillers. The most important component of the material is xonotlite, which by itself is a very good insulation material. As the xonotlite, in practice, synthetic xonotlite is used, which is obtained in the form of felted globules in the most frequently employed process. However, according to the invention, needle-shaped materials may also be employed, such as is obtained, for example, as a by-product in the processing of the spherical felted xonotlite.

The combination of xonotlite with the aluminous cement according to the invention produces the required optimum endothermic and insulating properties. Thus, the xonotlite becomes dehydrated only at about 800 °C, being converted into wollastonite. This dehydration is a strongly endothermic reaction and consumes much energy. The wollastonite formed thereby has a theoretical melting point at 1530 °C. The combination of wollastonite and cured aluminous cement results in a minimization of shrinking and thus prevents the risks due to cracking during shrinking. Thus, the fire protection and insulation make use of various phase transitions and the dehydration of the cured aluminous cement and xonotlite, retaining the spatial structure and mechanical stability.

Preferably, the material is employed in the form of prefabricated smooth or bent plates. However, it may also be sprayed on in a per se known manner, in which

case it has to be taken care that the required minimum thickness of the coating is ensured and that the material adheres well to the substrate. The material according to the invention may also be used as a repair and joint mortar to repair broken off or burnt out parts of the material, ensuring the same or comparable properties of the repaired areas.

In the following Examples, the product according to the invention will be illustrated in more detail. From the comparative experiments with products of the prior art, it can be seen that the material according to the invention has clearly superior properties which could not be foreseen from the prior art.

Example 1

The compositions of mixtures for preparing the product according to the invention are summarized in the following Table I.

Table I

Compositions (according to the invention)							
Materials	casting	casting	casting	casting	casting	casting	filter press
	TB008	TB009	TB010	TB112	TB118	TB119	TB511
Aluminous cement	weight parts	weight parts	weight parts	weight parts	weight parts	weight parts	weight parts
Lafarge fondu	100			100			100
Secar 51®		100			100		
Secar 71®			100			100	
Xonotlite suspension (10% dry xonotlite in water)	160	160	160	160	160	160	225
Wollastonite				15	15	15	15
Vermiculite (0-2 mm)	12	12	12				
$Al(OH)_3$				35	35	35	35
Exp. pearlites				5	5	5	5
Bentonite							4.5
Cellulose (dry)				0.5	0.5	0.5	1.2
Glass fibers				2.5	2.5	2.5	2
PVA fibers							2
Plasticizing agent (35% in water/Plastijn sol.)				0.4	0.4	0.4	
Density	0.955	0.938	0.973	1	1	1	1

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The compositions of the comparative mixtures are summarized in Table II.

Table II

Comparative composition (weight parts)			
	casting	casting	casting
	TB011	TB042	TB043
Aluminous cement			
Lafarge fondu (CFL)	100	100	100
Wollastonite	60		
Exp. clay 0-2 mm		40	
Exp. clay 2-4 mm		80	
Glass spheres (Poraver®) 0.25-0.5 mm			40
Glass spheres (Poraver®) 1-2 mm			60
Water	200	100	100
Kaolin	140		5
Gypsum		50	50
Density	1.22	1.2	0.85

The product TB011 is about the same as the commercial product Firebarrier* 135.

The product Promatect* H (briefly PtH) is prepared by the Hatschek process and cured in an autoclave (thickness of the plates 25 to 27 mm, density 0.9 to 1.0). Examination of these materials according to the Dutch test method yielded the values according to Figures I to V. It can be seen therefrom that the products TB008, TB112, TB118, TB119 and TB511 according to the invention have clearly better properties as compared to the comparative products TB042, TB043 and PtH. The test results of the comparative product TB011 were even worse than those of

* trade-mark

residual moisture of 2.5%. The company TNO, an internationally known independent test laboratory in Holland, tested them for their fire-protecting properties according to the directions RWS (Rijkswaterstaat) in which a hydrocarbon fire is simulated.

For comparison, a layer with a thickness of 38.5 mm of the commercial product FireBarrier 135® (approximately corresponding to the composition TB011) was examined. The layer had a density of 1.257 kg/m^3 and a residual moisture of 7.5%. This water results in a somewhat longer lasting fire protection. The test results are summarized in Figure V. They show that the material according to the invention meets the minimum requirements already at a layer thickness of only 15 mm, i.e., to remain below 380 °C after 120 min on the backside, i.e., the contact area with the cement. The comparative product FireBarrier 135® achieves this object only at a layer thickness of 38.5 mm and a three times higher moisture content.

At layer thicknesses of 25 and 30 mm, the material according to the invention provides an essentially better fire protection. TNO already established a fire protection of at least three hours.

CLAIMS:

1. A fire-protection material for constructions made of concrete and prestressed concrete, in the form of prefabricated plates or sprayed-on and cured coatings prepared from a hydraulically curing composition containing aluminous cement, wherein the cured material contains less than 5% by weight of ettringite, characterized in that the composition contains from 50 to 200 weight parts of aluminous cement and from 10 to 250 weight parts of xonotlite in the uncured state, the xonotlite being in the form of felted globules.

2. The material according to claim 1, characterized by being prepared from as many or twice as many weight parts of hydraulic binder as there are weight parts of xonotlite.

3. The material according to claim 1 or 2, characterized by additionally containing at least one of Portland cement, fillers, fibers, curing accelerators, curing delayers, plasticizing agents and foaming agents, in the uncured state.

4. The material according to claim 3, characterized in that the curing composition contains at least one of wollastonite, tobermorite and aluminum hydroxide, as fillers.

5. The material according to any one of claims 1 to 4, characterized in that the curing composition contains light-weight fillers selected from the group consisting of pearlites and vermiculites.

6. The material according to any one of claims 1 to 5, characterized by containing fibers.

7. The material according to any one of claims 1 to 6, characterized by having a density of from 0.7 to 1.3 g/cm^3 in the cured state.

8. The material according to any one of claims 1 to 7, characterized by being in the form of prefabricated plates prepared by casting or filter pressing.

9. The material according to claim 8, characterized in that said plates are in a bent form.

10. The material according to any one of claims 1 to 7, characterized by being in a form for use in tunnels.

11. Prefabricated plate consisting of a fire-protection material according to any one of claims 1 to 9.

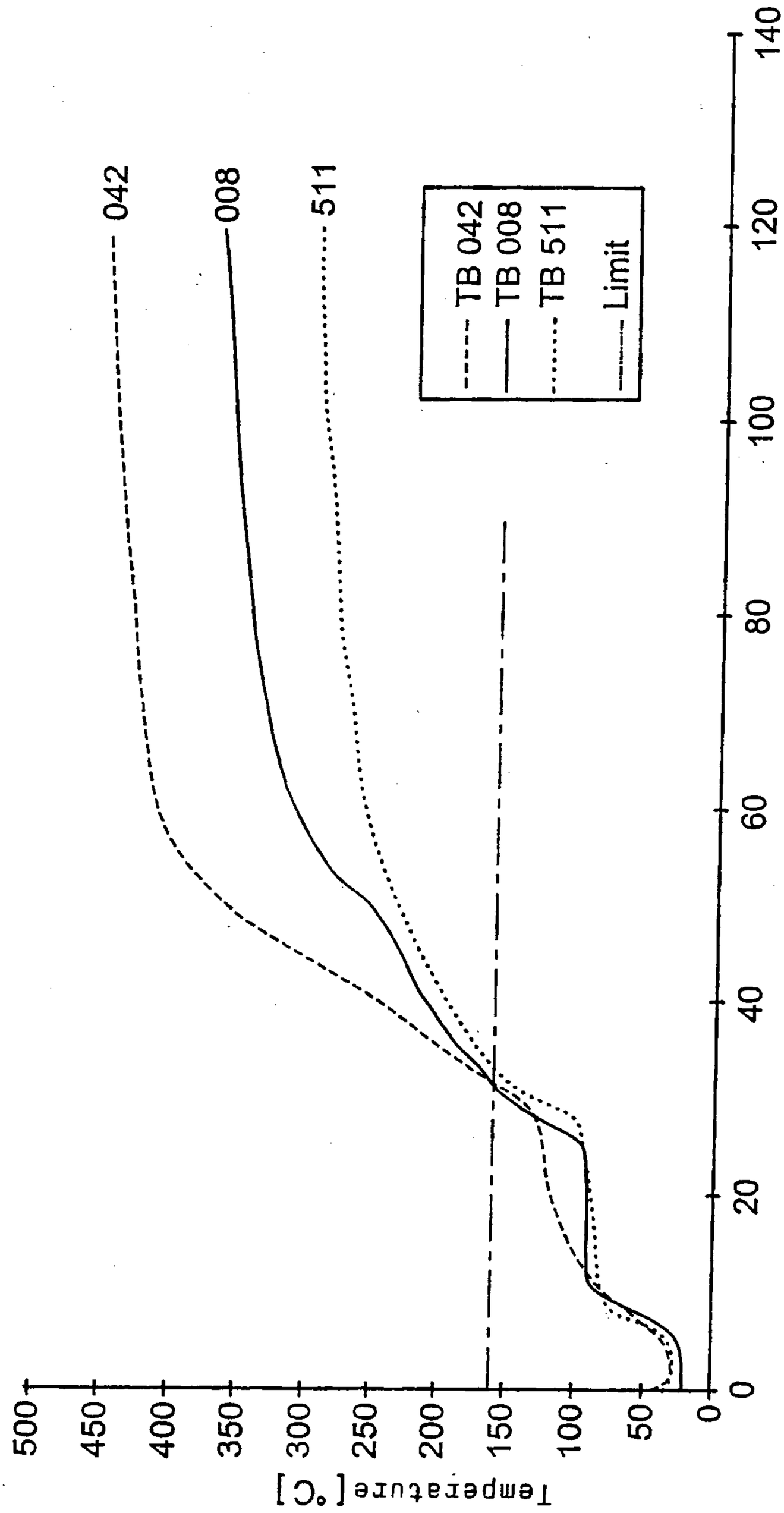

042
008
511
TB 042
TB 008
TB 511
Limit
140
120
100
80
60
40
20
0
[min]
500
450
400
350
300
250
200
150
100
50
0
Temperature [°C]

Fig.1

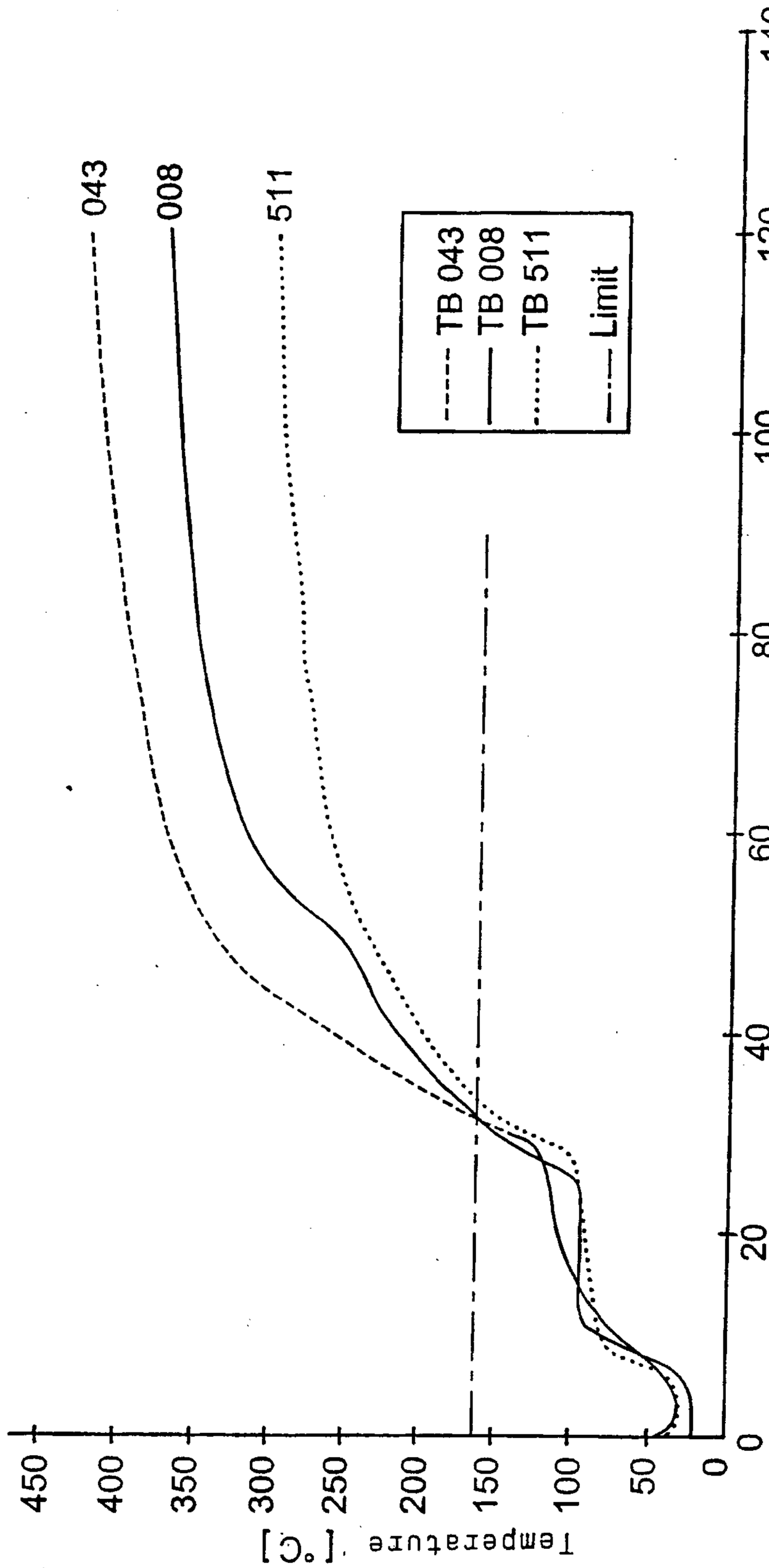

Temperature [°C]
450
400
350
300
250
200
150
100
50
0
[min]
0
20
40
60
80
100
120
140
043
008
511
TB 043
TB 008
TB 511
Limit

Fig.2

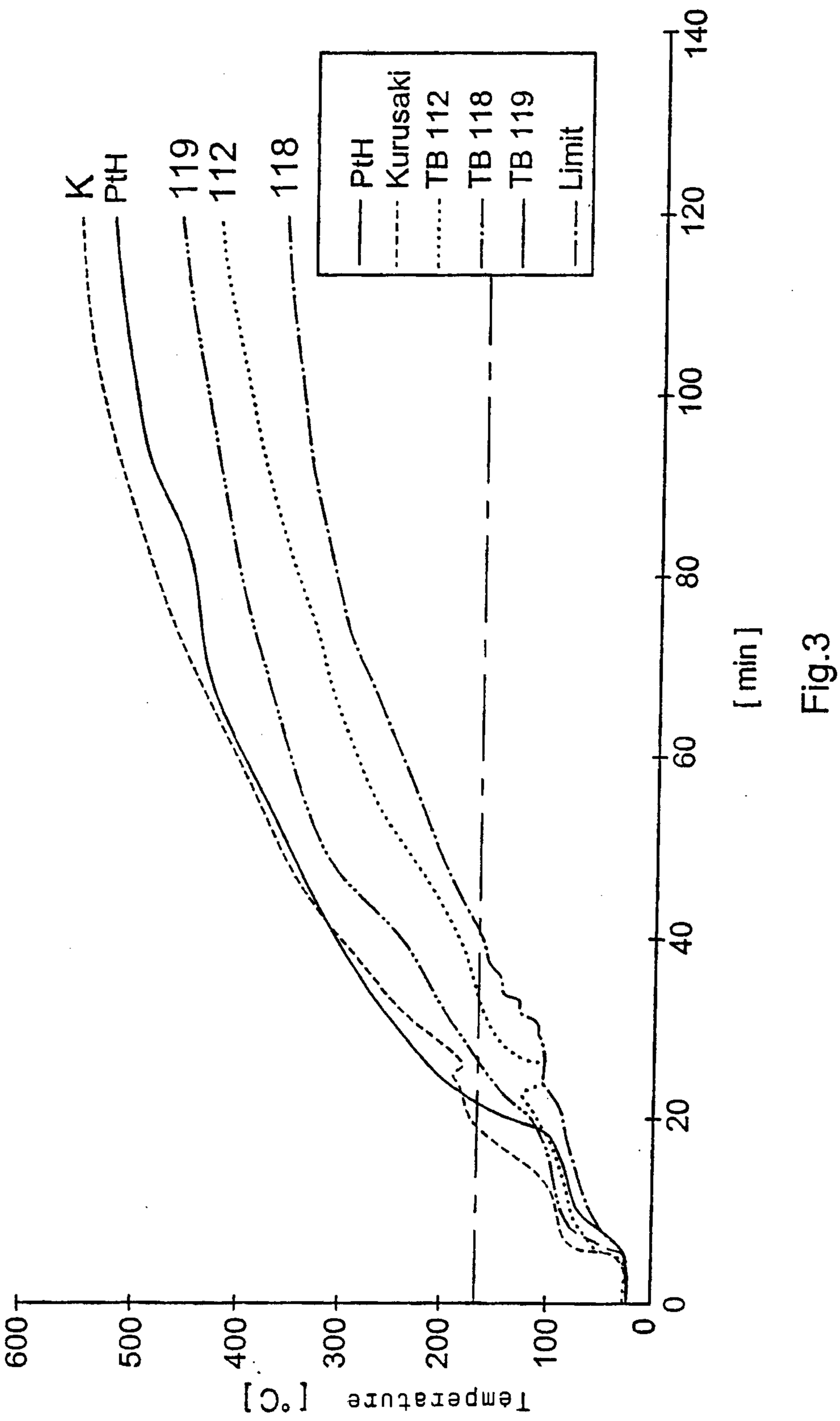

K
PtH
119
112
118
PtH
Kurusaki
TB 112
TB 118
TB 119
Limit
140
120
100
80
60
40
20
0
[min]
600
500
400
300
200
100
0
Temperature [°C]

Fig.3

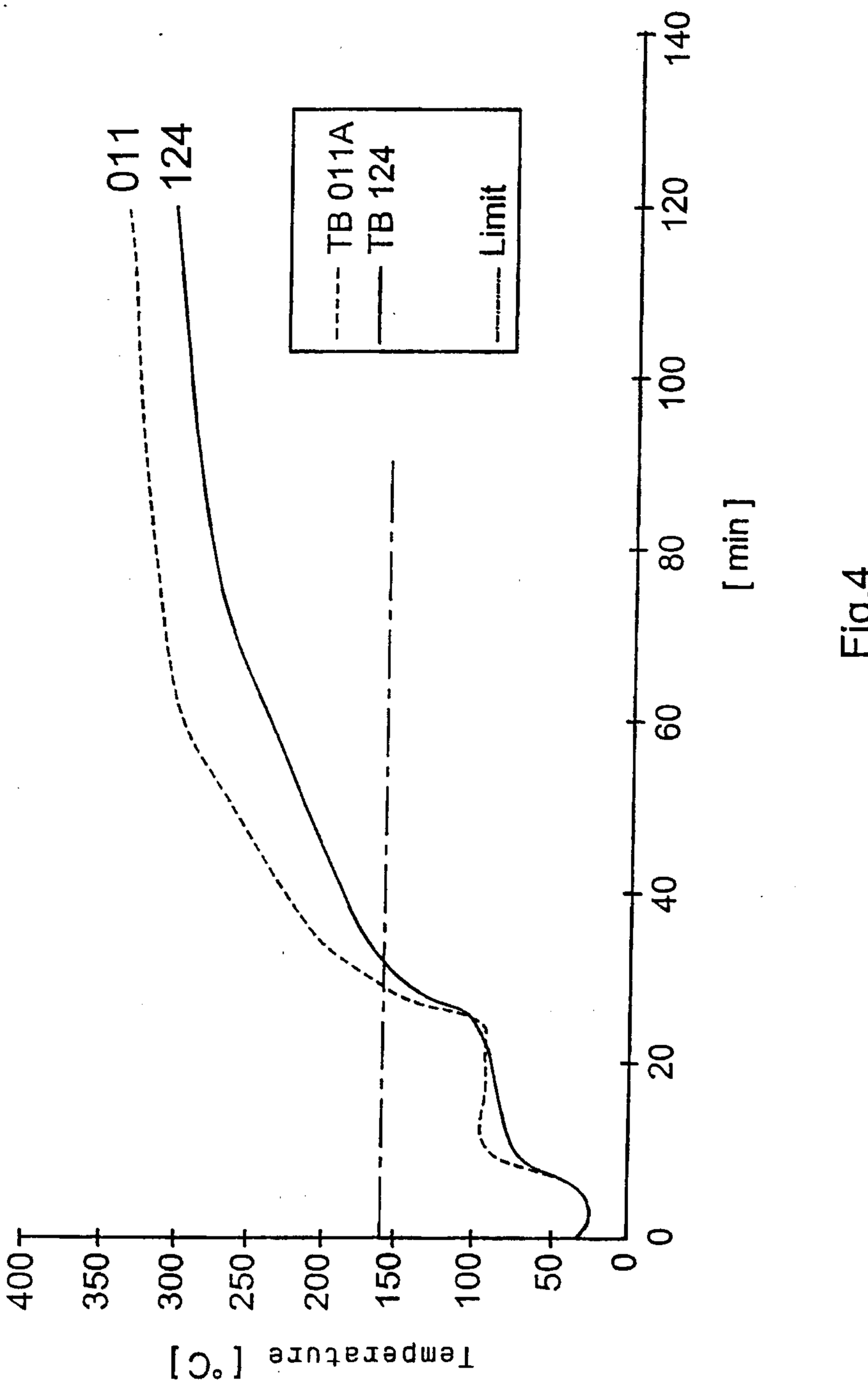

011
124
TB 011A
TB 124
Limit
Temperature [°C]
400
350
300
250
200
150
100
50
0
0
20
40
60
80
100
120
140
[min]

Fig.4

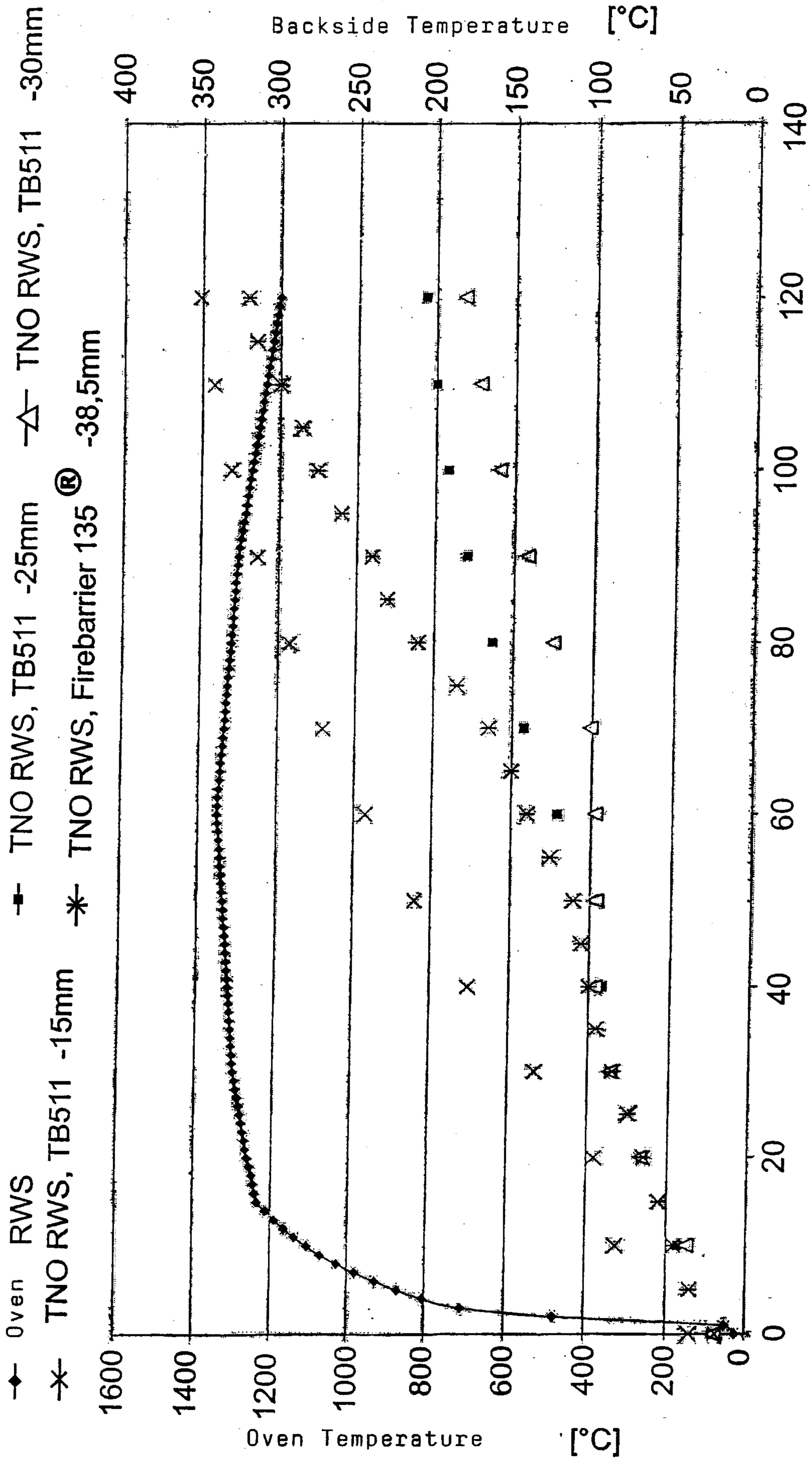

Backside Temperature [°C]
400
350
300
250
200
150
100
50
0
140
120
100
80
60
40
20
0
[min]
TNO RWS, TB511 -30mm
TNO RWS, TB511 -25mm
TNO RWS, Firebarrier 135 ®
TNO RWS, TB511 -38,5mm
TNO RWS, TB511 -15mm
Oven RWS
Oven Temperature [°C]
1600
1400
1200
1000
800
600
400
200
0

Fig.5