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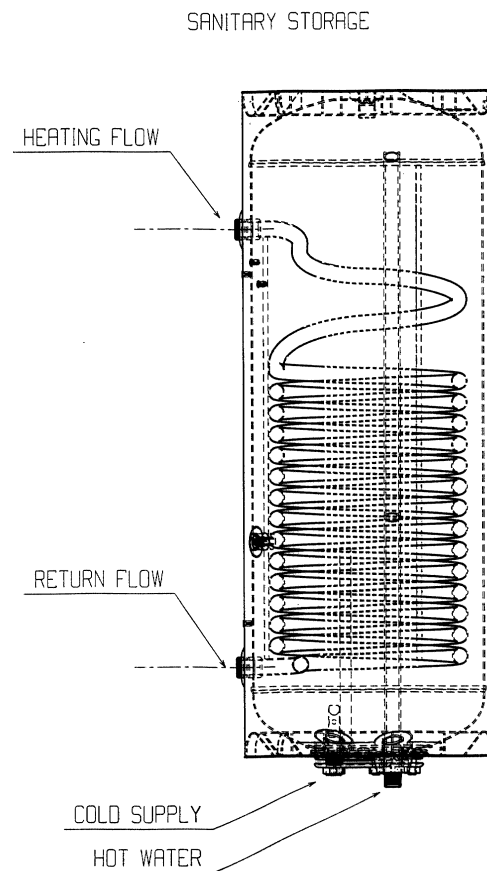
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(54) **Protection of the water-side surfaces of heat exchangers used in boilers and gas fired water heaters**

(57) In order to optimise the performance of boiler exchangers, avoiding the precipitation of calcium and magnesium carbonates, in addition to the fouling of the circuits caused by residual working products or by other foreign matters existing in the water network, while keeping drinkable the sanitary water produced according to the WRC standards, IABER S.p.A. has developed a treatment with particular fluorurated resins for the exchange surfaces.

Such resins adhere to metallic surfaces thus creating a few microns thick coating limiting the adhesion of limestone and of the deposits existing in heating circuits.



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Description

1. State of Art

[0001] All heat exchangers producing hot water, are subject to limestone precipitation of calcium and magnesium carbonates and to fouling of the circuits due to residual working products or other foreign matters present in the water network.

[0002] Besides, in case water contains some particular additives (for instance glycoles), the migration of metallic ions (Copper, Aluminium, Stainless Steel) may occur. The corrosion of metallic surfaces is always potentially possible.

[0003] The precipitation of limestone is more significant, the higher is the water limestone contents (hardness of water), the higher is the water heating and the longer is the time water remains at high temperature.

[0004] The fouling due to limestone and solid foreign matters present in the network occurs in different types of exchangers, such as:

- Bi-thermic exchangers for the combined production of hot water both for ambient heating and for sanitary (Fig. 1).
- Primary exchangers for the production of hot water for ambient heating only (Fig. 2).
 - Plate-type exchangers for the production of sanitary hot water (Fig. 3).
 - Storage vessels for the production and the storage of sanitary hot water (Fig. 4).
 - Additional storage systems for sanitary hot water.
 - Exchangers for water heaters.

[0005] The exchangers intended for the production of sanitary hot water (plate-type, primary exchangers, vessels, sanitary water tanks and bi-thermic exchangers) shall keep drinkable the sanitary water produced according to WRC standards.

[0006] The metals used for exchangers are, according to the type:

Copper (Cu DHP, CU OF, SE CU)
Stainless Steel (AISI 316L, AISI 304)
Aluminium

[0007] The water-diluted product has a viscosity comparable to water viscosity and is such as to fill all the interstices of the exchangers.

[0008] The exchangers nowadays on sale need to be frequently cleaned with specific acids to remove limestone crusts and dirt deposits causing in the run of time the obstruction of the passages and the thermal unbalance of the exchangers.

2. Description of the invention

[0009] In order to limit the above undesired effects, a procedure has been developed to treat the exchange surfaces with particular fluorurated resins. Such resins are provided with functional groups that adhere to the metallic surfaces to create a few microns thick coating limiting the adhesion of limestone and of the deposits present in heating circuits.

[0010] The peculiar features of the treatment, i.e. the anti-adhesion of limestone on the coated surfaces, have been checked both at IABER S.p.A. test laboratory (Ann. 1) and at the laboratory of the resin Manufacturer (Ann. 2), and through tests "on the field".

[0011] The performance of the thermal exchange and the hydraulic characteristics of the exchangers are not at all modified by the treatment.

[0012] The resin coating treatment is performed as follows. (diagram)

[0013] The water-diluted product has a viscosity comparable to water viscosity and such as to fill all the interstices of the exchangers.

3. Innovations introduced by the invention

[0014] The treatment of exchangers and vessels with fluorurated resins allows to overcome one of the weakest points of exchangers i.e. a reduced performance in the run of time due to the deposit of limestone and dirt present in the network. Specifically, thanks to this treatment, the circuits obstructions due to the effects of limestone and of a variety of residual working products are reduced and, therefore, the useful life of the same exchangers in compliance with specifications is extended.

[0015] Particularly, limestone keeps on precipitating during the water heating but, when precipitated, it does not adhere firmly to walls. On the contrary, it is eliminated by the same water stream. Similarly, thanks to the anti-adhering characteristics of the treatment, foreign matters in water (dirt and residual working products) do not fix to the exchangers walls but they slide away together with the water stream.

[0016] Moreover, the surface protection from such resins reduces the migration of metallic ions in water, the corrosion of the same metals and assures a higher water sanitation coming into contact with the water-side surfaces.

4. Patent Right Claims

[0017] The protection we claim with patent shall cover the application procedure of fluorurated products with low viscosity on the metallic surfaces made of Copper (CU DHP, CU OF, SE CU), Aluminium and Stainless Steel (AISI 316L, AISI 304) of the heat exchangers and vessels used for the production of sanitary hot water and ambient heating in storage or instantaneous gas-fired wall boilers and in water heaters.

[0018] The effect of the treatment is:

1. to limit the limestone deposit;
2. to limit the deposit of residual working products;
3. to keep unaltered the sanitation characteristics of the produced sanitary water
4. to keep unaltered the thermal exchange characteristics.

5. Laboratory tests carried out by IABER S.p.A.

[0019] Limestone tests have been carried out on treated vessels boiling the same quantity of water on a camp stove:

1. VESSEL No. 1 : Heat-treated Copper without special treatments
2. VESSEL No. 2 : Green Teflon SR43F coated Copper
3. VESSEL No. 3 : Ausimont Silane coated Copper

REMARKS:

[0020] Limestone deposits occur in Vessels No. 1 and No. 2, which do not detach from the walls.

[0021] In Vessel No. 3 the limestone patina does not deposit on the walls and with the addition of fresh water the limestone solution dissolves.

6. Laboratory tests carried out on account of IABER S. p.A.

[0022] The coating with functional perfluoropolyetheric products has been laid on some copper plates, in compliance with ordinary procedures.

[0023] The product has been applied by dip-coating with the following treatment formulas:

1. 1-Phosphate
2. 5-Phosphate
3. 1-Silane
4. 5-Silane

[0024] Copper test specimen has been plunged into the compounds for 10 minutes before heat-treatment:

- Heating at T = 80°C for 7 minutes
- Heating at T = 65°C for 40 minutes
- Heating at T = 160°C for 12 minutes

[0025] Subsequent to the preparation of the specimen, some measurements of static and dynamic contact angle versus water, hexadecane, dodecane, decane and octane were carried out. Only the results relevant to the measurement of the static contact angle versus water carried out before limestone deposition, after deposition and after washing under cold tap water are herein reported.

Contact angle measurements for treated/untreated copper specimen, before limestone deposition (table 1)

Contact angle measurements for treated/untreated copper specimen, after limestone deposition:

[0026] A calcium bicarbonate solution has been prepared. This is more soluble in water than the calcium carbonate (limestone) that tends to form and deposit at temperatures higher than 50°C. The treated/untreated specimen have been plunged into these boiling solutions for 3 hours. At the end of this time, the limestone deposit on all specimen was recorded; on specimen treated with Silane, however, the amount of the deposit was the lowest (also on phosphate a certain effect was noted). Here below the measurements of static contact angle versus water after limestone deposition under the described conditions are recorded.(table 2)

Contact angle measurements for treated/untreated copper specimen, after washing under tap flowing water:

[0027] Test specimen have been washed under a stream of cold tap-water for few seconds; after this time specimen have been stove-dried for 15 minutes and then the static contact angle versus water was measured again (table 3)

[0028] The best treatment proved to be that with silanes (5-Silane specimen) showing:

- lower limestone deposit
- greater easiness in removing limestone
- lower copper oxidation

Claims

1. Low viscosity resins are used.
2. It is suitable both for metallic surfaces made from Copper (CU DHP, CU OF, SE CU) and for Aluminium and Stainless Steel (AISI 316L, AISI 304).
3. It can be applied to heat exchangers, to vessels, to storage tanks used for heating in wall or base gas-fired boilers and to water heaters.
4. It limits the limestone deposit.
5. It limits the deposit of residual working products.
6. It keeps the characteristics of the sanitary water produced unaltered.
7. It keeps the characteristics of the thermal exchange unaltered

8. It prevents the migration of metallic ions.

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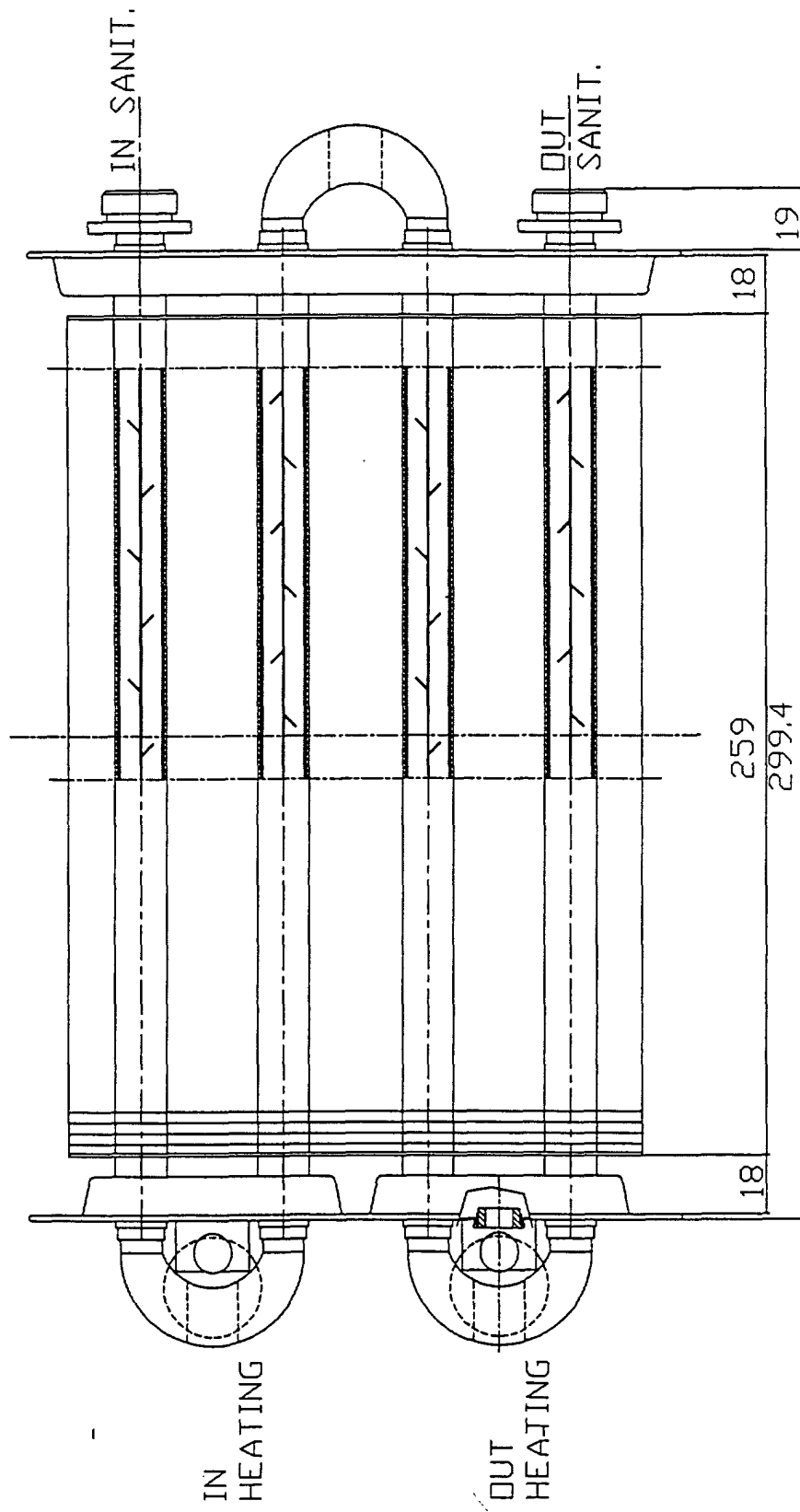
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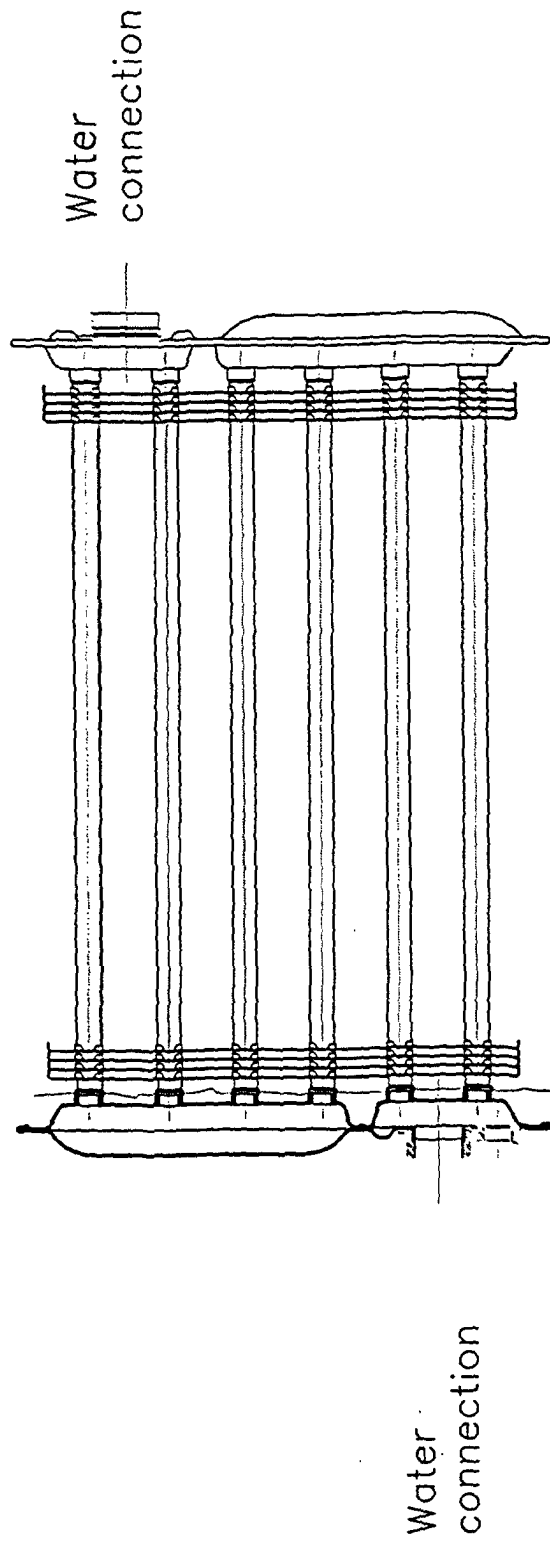
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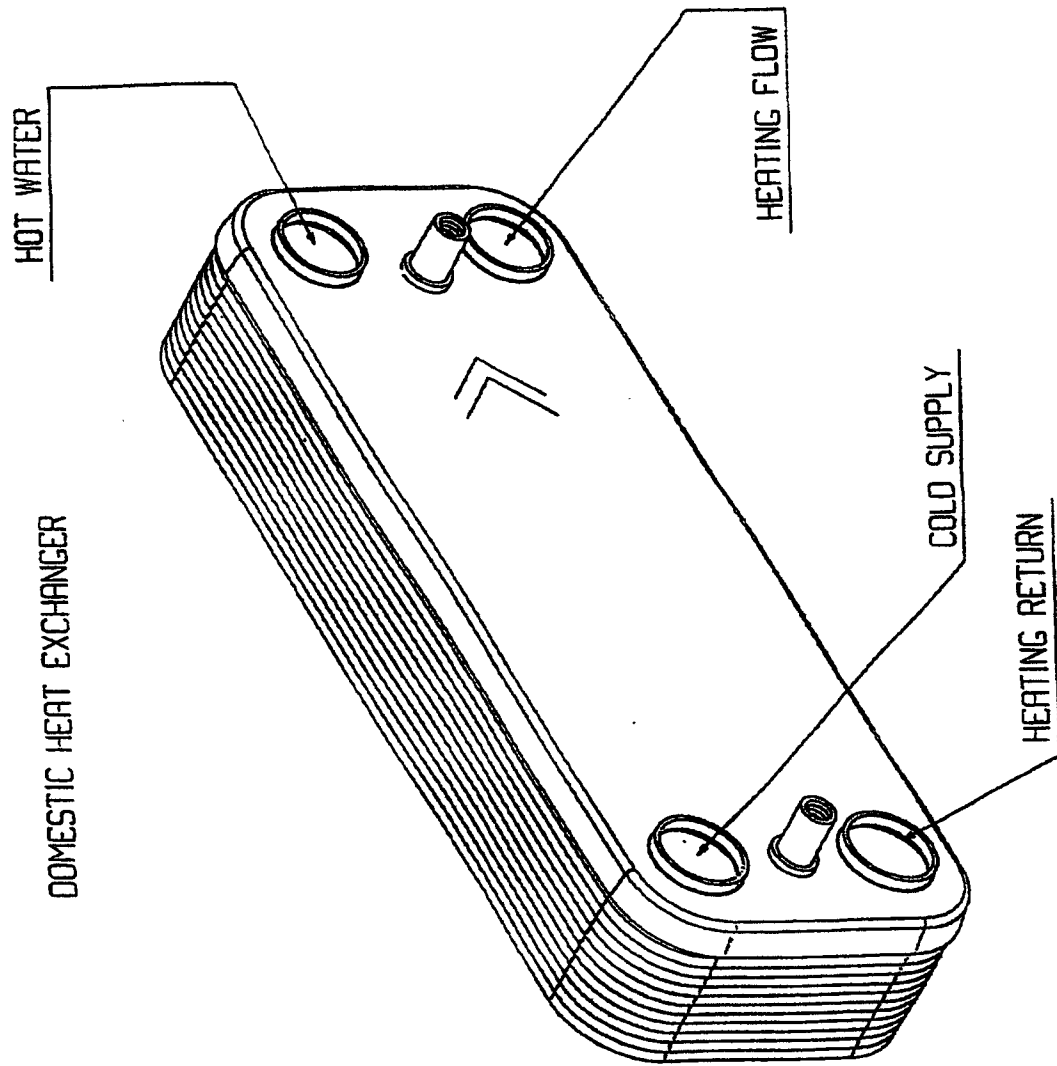
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Bithermic Heat Exchanger

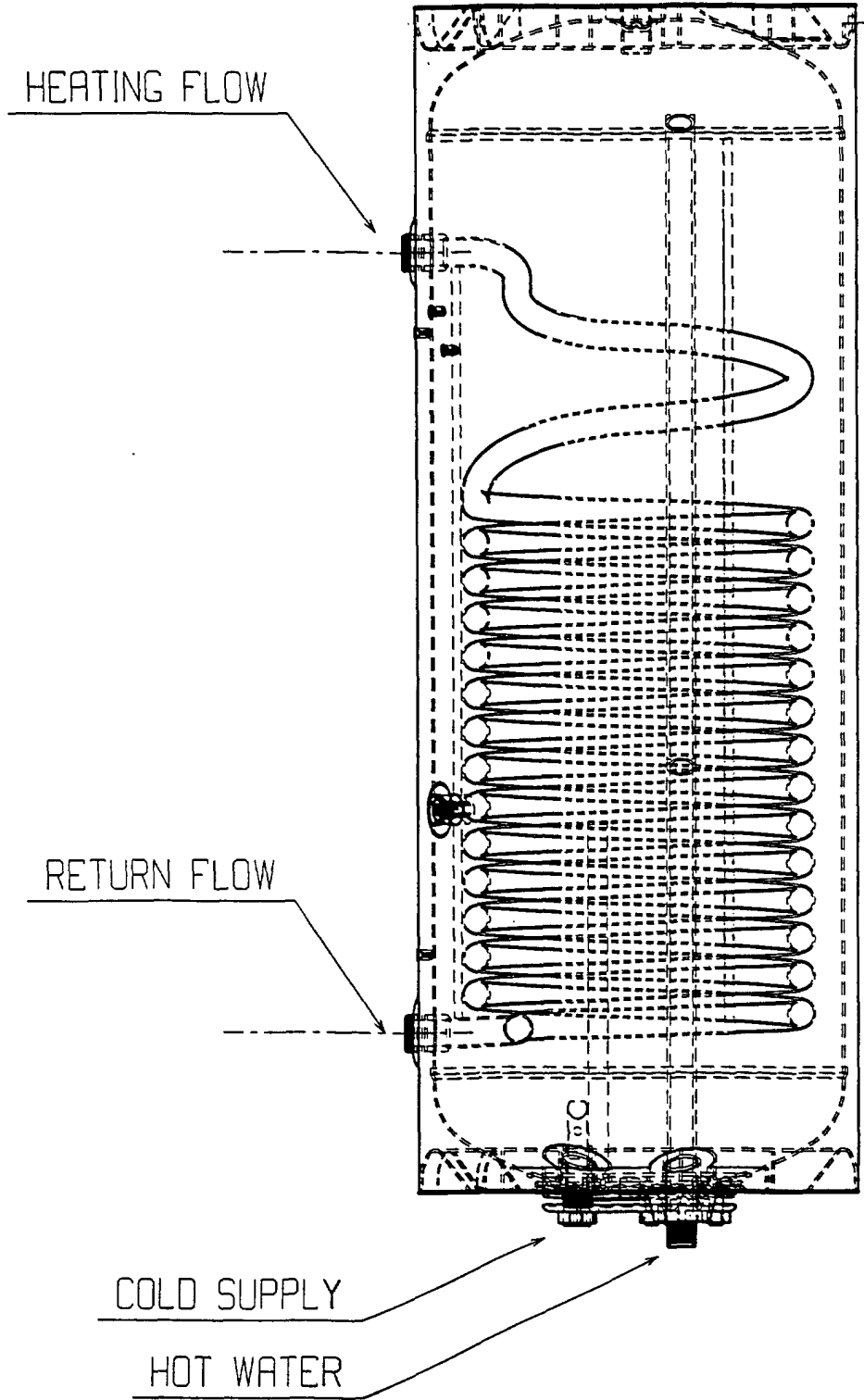


Primary Heat Exchanger





SANITARY STORAGE



DIAGRAM

stock
resin

H2O dissolve stock product
 in water

 watery product
 for use

 fill the circuit to
 process and
 take for necessary
 time

 empty the processed
 circuit flowing by
 compressed air

 is possible cook the
 piece in the oven

Samples	Angle of contact	Angle of static contact vs water for white
1 phosphate	113°	
5 phosphate	115°	
1 silane	110°	80°
5 silane	110°	

TAB 1

Samples	Angle of contact	Angle of static contact vs water for white
1 phosphate	60°	
5 phosphate	90°	
1silane	80°	40°
5 silane	92°	

tab. 2

Samples	Angle of contact	Angle of static contact vs water for white
1 phosphate	109°	
5 phosphate	110°	
1 silane	110°	56°
5 silane	110°	

tab.3



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PARTIAL EUROPEAN SEARCH REPORT

Application Number

which under Rule 45 of the European Patent Convention EP 00 20 0746 shall be considered, for the purposes of subsequent proceedings, as the European search report

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.7)
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A	WO 92 16310 A (ALFA LAVAL THERMAL) 1 October 1992 (1992-10-01) * the whole document *		
	-/--		
			TECHNICAL FIELDS SEARCHED (Int.Cl.7)
			B05D F28F
INCOMPLETE SEARCH			
<p>The Search Division considers that the present application, or one or more of its claims, does/do not comply with the EPC to such an extent that a meaningful search into the state of the art cannot be carried out, or can only be carried out partially, for these claims.</p> <p>Claims searched completely :</p> <p>Claims searched incompletely :</p> <p>Claims not searched :</p> <p>Reason for the limitation of the search: see sheet C</p>			
Place of search	Date of completion of the search	Examiner	
THE HAGUE	22 September 2000	Brothier, J-A	
CATEGORY OF CITED DOCUMENTS			
<p>X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document</p>		<p>T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document</p>	

EPO FORM 1503 03.82 (P04C07)



Claim(s) not searched:

1-8

Reason for the limitation of the search:

The wording, form and content of the claims is such that a lack of clarity within the meaning of Article 84 EPC arises to such an extent as to render a meaningful search of the claims impossible. The claims neither define the matter for which protection is sought in terms of any technical features of the invention nor do they indicate which category or kind of claim is intended to define such protection, Rule 29(1) EPC, first sentence; refer also to rule 29(2) EPC.

Consequently, the search has been carried out for those parts of the application which might be regarded as clear, disclosed and supported, namely an activity (method or use) comprising the step of treating the surface of metallic heat exchangers and/or boilers with fluorinated resins having functional groups and diluted in water in order to reduce deposition of limestone and other deposits present in heating circuits.



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PARTIAL EUROPEAN SEARCH REPORT

Application Number
EP 00 20 0746

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EPO FORM 1503 03.82 (P04C10)

**ANNEX TO THE EUROPEAN SEARCH REPORT
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EP 00 20 0746

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For more details about this annex : see Official Journal of the European Patent Office, No. 12/82