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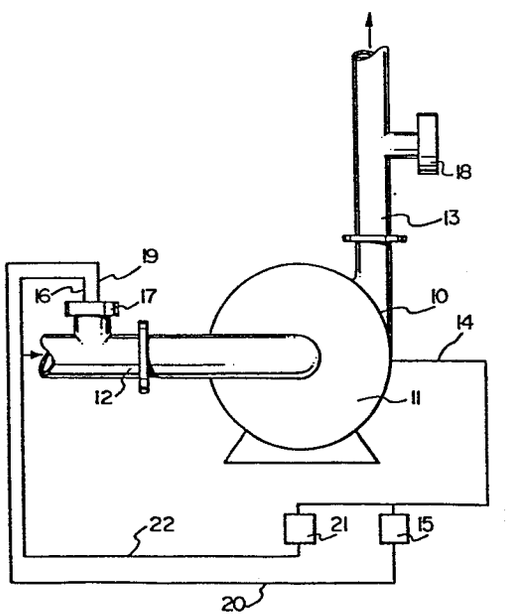
(54) Electrochemical pump protection.

(57) A pump is provided herein for pumping a corrosive aqueous solution. The pump includes (i) a stainless steel or carbon steel casing; (ii) an inlet limb connected to the stainless steel or carbon steel casing; (iii) an outlet limb connected to the stainless steel or carbon steel casing; (iv) means electrically connecting the stainless steel or carbon steel casing to a source of negative or positive DC voltage, thereby to induce the stainless steel or carbon steel casing to act as an anode or as a cathode as required; (v) at least one reference electrode secured within at least one of the inlet limb and the outlet limb; (vi) at least one counter electrode secured within at least one of the inlet limb and the outlet limb; and (vii) control means for impressing a protection potential to the stainless steel or carbon steel casing at a predetermined voltage of -800 $mV_{Ag/AgCl}$ or more positive, the predetermined voltage being sufficient to draw the stainless steel or carbon steel casing into a zone of reduced corrosion. This structure protects the stainless steel or carbon steel casing of the pump from corrosion.



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1. BACKGROUND OF THE INVENTION

(i) Field of the Invention

This invention relates to a system and method for the protection of pumps by electrochemical means. More particularly, it is directed to a method and apparatus for protecting, from corrosion, stainless steel pumps used to pump agressive solutions in bleach plants or kraft pulping liquor lines.

(ii) Description of the Prior Art

Stainless steel is known to be generally resistant to corrosion due to a build-up thereon of passive films. However, such passive films are susceptible to localized breakdown, and this susceptibility is greatly enhanced in the presence of specific ions. The filtrate used in bleach plant washers generally contains oxidants, e.g., chlorine (Cl_2), chlorine dioxide (ClO_2), or hypochlorite (OCl^-) together with a considerable amount of chloride ions. Such filtrate can bring about localized passive film failure. The loss of protection leads to various modes of localized corrosion, the principal ones being crevice corrosion and pitting corrosion.

The corrosion environment in the chlorine and chlorine dioxide stages of a bleach plant is generally acidic, with a pH in the range of 1 to 7. Stainless steel pumps are therefore used to pump such liquids. The most common alloys of construction are 316L and 317L stainless steel or their equivalents.

The corrosion environment in the hypochlorite stage of bleach washers is generally alkaline, with a pH in the range of 8-11. Stainless steel pumps are therefore used to pump such liquids. The most common alloy of construction is 316L or equivalent stainless steel. It would be preferable to use 304L or equivalent stainless steel

since it is much cheaper than 316L stainless steel. However, 304L stainless steel has been largely unsuccessful for this use because of severe chloride crevice corrosion.

The corrosion environment in alkaline pulping liquor systems generally has a pH above 12 and may contain unsettled solids, e.g. carbonates and general dirt and debris from the wood chips. Both stainless steels and carbon steels are common materials of construction; however, it is most common to use 316L stainless steel for liquor pumps. These pumps suffer from erosion-corrosion brought about by the combined action of corrosive pulping liquor and erosion due to unsettled solids. It would be beneficial to control the corrosion component of this attack, thereby extending the life of alkaline liquor pumps.

Electrochemical corrosion control would seem to offer a solution to the widespread problems of crevice and pitting corrosion of stainless steels in the pumps used for pumping the corrosive solutions used in the aforesaid pulp mill environments. Many patents teach the concept of corrosion control, either by inducing passivity in the metal by anodic polarization techniques, or by cathodic polarization.

Amongst the prior patents dealing with the anodic polarization are: United States Patents Nos. 3,371,023 issued February 7, 1968; 3,375,183 issued March 26, 1968; 3,378,472 issued April 16, 1968; 3,379,629 issued April 23, 1968; 3,409,526 issued November 5, 1968; United States Patent No. 1,576,581 issued March 16, 1926, to Elmore et al; United States Patent No. 3,442,779 issued May 6, 1969 to Hoey; United States Patent No. 4,018,647 issued April 19, 1977 to Poyser; and United States Patent No. 4,036,716 issued July 19, 1977 to Hulthe.

Amongst the prior patents which relate to the application of cathodic protection of metal surfaces including precise control of the impressed current are: United States Patent No. 2,435,937 issued February 17, 1948 to MacTaggart et al; United States Patent No. 3,634,222 issued January 11, 1972 to Stephens, Jr.; United States Patent No. 3,692,650 issued September 19, 1972 to Kipps et al; and United States Patent No. 4,080,272 issued March 21, 1978 to Ferry et al.

A further improved electrochemical corrosion protection technique was taught in United States Patent No. 4,285,787 issued August 25, 1981 to A. Garner and L.H. Laliberte. That patent taught a method of electrochemical protection by cathodic polarization of a stainless steel member subjected periodically to varying concentrations of corrosive, oxidizing chloride ions, e.g., a partly submersed, rotating, stainless steel drum in a vat containing a corrosive oxidizing chloride containing bleach liquor. That method taught the essential step of impressing a protective potential to the stainless steel member, e.g., the drum, at a predetermined voltage in the range of -600 to +400 $mV_{Ag/AgCl}$, the predetermined voltage being sufficiently low to draw the stainless steel into a passive corrosion protection zone but not sufficiently low to draw it into a zone of uniform corrosion. Yet the application of this protection method to a stainless steel pump would not serve to provide corrosion protection to the pump.

2. SUMMARY OF THE INVENTION

(i) Statement of Invention

This invention now provides a pump for pumping an aqueous agressive chloride-ion-containing liquid. The pump includes a stainless steel casing, an inlet limb (either made of stainless steel and electrically isolated

from the stainless steel casing, or of glass-fibre reinforced plastic), which is connected to the stainless steel casing, and, an outlet limb (either made of stainless steel and electrically isolated from the stainless steel casing or of glass-fibre reinforced plastic), which is connected to the stainless steel casing. Means are included for electrically connecting the stainless steel casing to a source of DC voltage, thereby to induce the stainless steel casing to act as a cathode or anode. At least one reference electrode is secured within, and is electrically isolated from, the inlet limb and/or outlet limb. At least one counter electrode is secured within and is electrically isolated from the same inlet limb and/or outlet limb. Means to electrically connect the counter electrode to the source of DC voltage. Finally, control means are provided for impressing a protection potential to the stainless steel casing at a predetermined voltage of -800 $mV_{Ag/AgCl}$ or more positive. Such predetermined voltage is sufficient to draw the stainless steel casing into a passive corrosion zone, but is not sufficiently low to draw the stainless steel casing into a zone of uniform corrosion.

(ii) Other Features of the Invention

Because of the shape of the pump casing, it has been found that it is necessary to provide a working electrode (i.e., the pump) with two separate sets of reference electrode and counter electrode. One reference electrode and counter electrode set is placed at the pump inlet and the other reference electrode and counter electrode set is placed at the pump outlet. The exact combination of reference and counter electrodes used depends upon the aggressiveness of the solution being pumped. Successful protection is provided whether or not the system is in its pumping mode, and no damage occurs when the system is not in its pumping mode.

The invention also provides a pump and a method of protecting a pump comprising any novel feature or novel combination of features disclosed herein.

3. DETAILED DESCRIPTION OF THE INVENTION

There are various types of reference electrodes which may be used. Two types of the screw-in type, or of the breech-type holder. The reference electrode may be an Ag/AgCl insert which is epoxy potted, with a silicone seal, in titanium, nickel base alloy, stainless steel or synthetic plastic material, or it may be a saturated calomel electrode.

Similarly, the counter electrode may be of various types. Two such types are of the U-bend form, or of the cantilever form with a blow-out preventer. The counter electrode may be platinized niobium on copper, or it may be 316L stainless steel.

The pump is preferably provided with two coverplates, one on the suction side, the other on the pressure side. The coverplates may be of stainless steel, nickel base alloy or titanium, or of synthetic plastic material. If the coverplate is made from a synthetic plastic material, it is preferred that the coverplate be provided with a stainless steel backing plate. The coverplates may be situated on small side-arms set into the main process piping, preferably where the side arms are of the "T" or "Y" type.

The invention also provides a method of protecting a pump having a stainless steel casing, an inlet limb and an outlet limb, comprising the steps of: electrically connecting said stainless steel casing to a source of DC voltage, thereby to induce the stainless steel casing to act either as a cathode or anode; securing at least one reference electrode within at least one of said inlet limb and said outlet limb; securing at least one counter electrode within the same limb selected from said inlet limb and said outlet limb; and impressing a protection potential to said stainless steel casing at a predetermined voltage of -800 $mV_{Ag/AgCl}$ or more positive, said

predetermined voltage being sufficient to draw the stainless steel casing into a passive corrosion zone, but not being sufficiently low to draw said stainless steel casing into a zone of uniform corrosion, in situations where such corrosion is possible.

Experiments were conducted to investigate pump protection in both bleach plant, and chemical pulping, environments. A 316L type stainless steel laboratory pump was used, and experiments were carried out using simulated chlorine-stage and chlorine dioxide-stage bleach solutions, and a simulated white liquor. In each case, the protection obtained was assessed by measuring potentials within the pump casing at various locations by means of salt bridges. Two reference electrode-counter electrode sets were used, one at the pump inlet and one at the pump outlet. A potentiostat was used, with the reference electrode at the pump inlet being employed as the control electrode.

Chlorine-stage tests were carried out with chlorine concentrations ranging from 0 to 125 ppm. Typical results are shown in Table I. Without protection, potentials across the pump casing were in the range +370 to +600 $mV_{Ag/AgCl}$. When protection was applied with a -250 $mV_{Ag/AgCl}$ set point, the potentials were depressed into the range -250 to -100 $mV_{Ag/AgCl}$, the value depending on exact location within the pump and the chlorine concentration. The results in Table I indicate that, as the chlorine concentration increased, the potentials within the protected pump became more positive. Even for very high Cl_2 concentrations, however, potentials within the pump were kept at, or below -100 $mV_{Ag/AgCl}$.

Table I: Protection Potential Distributions Within the Test Pump Casing when Running Under Chlorine-Stage Conditions

Chlorine (ppm)	Measured Potential, versus Ag/AgCl		
	Pump Inlet (mV)	Impeller Casing (mV)	Pump Outlet (mV)
0	-250	-246	-251
51	-250	-140	-232
85	-250	-103	-230
125	-250	-100	-220

In order to verify that the potentials obtained within the protected pump did, in fact, correspond to reduced corrosion, corrosion coupon tests were carried out at selected potentials, using similar solutions, for Types 316L and 317L stainless steels. Results are shown in Table II, for a chlorine concentration of 50 ppm.

Table II. Effect of Potential on Localized Corrosion of Types 316L and 317L Stainless Steels in Simulated Chlorination Stage Washer Filtrate

Potential $(mV)_{Ag/AgCl}$	Number of Crevice Sites Initiated	
	316L	317L
+300	20	20
+200	20	11
+100	17	4
0	1*	0
-100	0*	0
-200	0*	0

* general dissolution or discolouration

For 316L, localized corrosion is effectively prevented when at potentials more negative than +100 $mV_{Ag/AgCl}$; some general corrosion is experienced but this is far less damaging than localized attack. For 317L, crevice corrosion is similarly eliminated by holding at potentials more negative than +100 $mV_{Ag/AgCl}$ with the additional advantage that no general dissolution occurs.

Results of tests done with the pump in chlorine dioxide stage conditions are shown in Table III. Without protection, potentials within the pump casing lay in the range +380 to +600 $mV_{Ag/AgCl}$. When protection was applied with a -250 $mV_{Ag/AgCl}$ set point, these potentials fell until they were in the range -250 to +310 $mV_{Ag/AgCl}$, the exact value depending on pump casing location and chlorine dioxide concentration.

Table 3. Protection Potential Distributions Within the Test Pump Casing when Running Under Chlorine Dioxide-Stage Conditions

Chlorine Dioxide (ppm)	Measured Potential, versus Ag/AgCl		
	Pump Inlet (mV)	Impeller Casing (mV)	Pump Outlet (mV)
0	-250	-203	-210
44	-250	+221	- 96
103	-250	+308	- 71

To confirm that corrosion was obtained within the pump casing, a second set of corrosion coupon tests were carried out. Results are shown in Table IV. It should be noted that the tests are concerned only with Type 317L or equivalent stainless steel, as this is generally the minimum grade used in bleach plants for chlorine dioxide stage pumps.

Table IV. Effect of Potential on Localized Corrosion of Type 317L Stainless Steel in Simulated Chlorine Dioxide Stage Washer Filtrate

Potential $(mV)_{Ag/AgCl}$	Number of Crevice Sites Initiated 317L
+400	20
+300	11
+200	1
+100	1
0	0

Table IV shows that the potential of a Type 317L stainless steel has to be brought below +300 $mV_{Ag/AgCl}$ to halve the number of crevice sites initiated. Comparison of this data to that in Table III shows that significant protection of a 317L type pump casing will be achieved, even though the net change in potential at the impeller housing position is relatively small.

A third set of experiments was carried out using a synthetic white liquor. Results are shown in Table V. With no protection, potentials within the pump casing were at about -860 to -890 $mV_{Ag/AgCl}$. With protection, and for a -800 $mV_{Ag/AgCl}$ set-point, potentials lay within the range of -800 to -790 $mV_{Ag/AgCl}$.

Table V. Protection Potential Distributions Within the Test Pump Casing when Running with White Liquor

Test Condition	Measured Potential, versus Ag/AgCl		
	Pump Inlet (mV)	Impeller Casing (mV)	Pump Outlet (mV)
Without Protection	-882	-860	-880
With Protection	-800	-788	-801

Complementary weight loss tests in the white liquor were carried out to confirm that corrosion protection was obtained. At -900 mV s.c.e. a weight loss rate of 14 mg/cm^2/year was obtained, compared to 5.5 mg/cm^2/year at -800 mV s.c.e. These results show that the corrosion rate was reduced by almost two-thirds by the application of protection to the pump.

4. DESCRIPTION OF PREFERRED EMBODIMENTS

(i) Brief Description of the Drawings

In the accompanying drawings, the single figure is a schematic illustration of the protected pump of one embodiment of this invention for pumping an aqueous chloride-ion-containing liquid or chemical pulping liquor.

(ii) Detailed Description of the Drawing

As seen in the drawing, the pump 10 includes a stainless steel casing 11 to which is connected an inlet limb 12 and an outlet limb 13. A line 14 electrically connects the stainless steel casing 11 to a source of DC voltage 15, which is so connected as to induce the stainless steel casing 11 to act either as an anode or as a cathode as required. As shown, a reference electrode 16 is secured to coverplate 17 in the inlet limb 12, although, as described above, at least one such reference electrode may be secured within at least one of the inlet limb 12 or the outlet limb 13, e.g. within coverplate 18. As shown, a counter electrode 19 is secured within coverplate 17 in inlet limb 12, although, as described above, at least one counter electrode 19 would be secured to the same coverplate, e.g. 17 and/or 18 to which the reference electrode 16 is secured. A line 20 electrically connects the counter electrode 19 to the source of DC voltage 15. Control means 21 are electrically connected to the source of DC voltage 15, in order to impress a protection potential to said stainless steel casing at a predetermined voltage of -800 $mV_{Ag/AgCl}$ or more positive. A line 22 electrically connects the reference electrode 16 to the control means 21. As disclosed above, that predetermined voltage is sufficient to draw the stainless steel casing into a passive corrosion zone.

In the preferred embodiment of this invention, each electrode coverplate (17,18) requires one reference electrode (16) and one counter electrode (19). It is preferred that, if only one counter electrode (19) and one reference electrode (16) be used, they be located on the same side of the pump casing (11); if they are located on opposite sides of the pump casing (11), gross negative potentials can be generated, especially when the pump is not operating.

The reference electrode (16) can be of the screw-in type. For bleach plants, this electrode can be an Ag/AgCl insert which is epoxy mounted with a silicone seal in titanium, INCONEL 625 or AVESTA 254 SMO. [INCONEL 625 is a registered trade mark of Huntington Alloys, Inc. AVESTA 254 SMO is a registered trade mark of Avesta Jernverks AB]. Alternatively, it may be KYNAR bodied, with the electrode mounted in a breech-type holder. [KYNAR is a registered trade mark of Pennwalt Corporation]. In alkaline pulping liquor, a suitably designed saturated calomel reference electrode (16) is preferred.

For bleach plants, the counter electrode (19) is preferably platinized niobium on copper and, in alkaline pulping liquor, the counter electrode is preferably Type 316 stainless steel. In physical form, it may be a U-bend, exiting through two CONAX glands, or a cantilever, with blow-out prevention collar, exiting through one CONAX gland. [CONAX is a registered trade mark of Conax Corporation]. This substantially eliminates blow-out danger.

In the bleach plant, the coverplate (17,18) may be metallic or non-metallic. If metallic, the coverplate should preferably be AVESTA 254 SMO stainless or similar, steel, HASTELLOY-C or titanium. [HASTELLOY-C is a registered trade mark of Cabot Corporation]. If non-metallic, it should preferably be a polyvinyl chloride or KYNAR

plate with a stainless steel backing plate provided with O-ring seals. A polymeric plate without a stainless steel backing may be adequate if it meets strength requirements. In alkaline pulping liquor, a Type 316L stainless steel coverplate is preferred. The pump should have two coverplates (17,18), one on the suction side (12) and one on the pressure side (13). To minimize vibrational and/or erosion problems on the electrodes, the coverplates should ideally be situated on small side arms of the "T" (type as shown) or "Y" type, set into the main process piping. If environmental considerations permit, the potentiostat could be mounted near or on the coverplates.

SUMMARY

From the foregoing description, one skilled in the art can easily ascertain the essential characteristics of this invention, and without departing from the spirit and scope thereof, can make various changes and modifications of the invention to adapt it to various usages and conditions. Consequently, such changes and modifications are properly, equitably and "intended" to be, within the full range of equivalence of the following claims.

Among the features of the embodiments of the invention descibed above which are preferred features and may be made the subject of further claims to be added in in due course to the 10 claims with which this application is filed, are the following:

10. The pump of claim 1 wherein said reference electrode is of the breech-type holder.

11. The pump of claim 9 wherein said reference electrode is an Ag/AgCl insert which is epoxy potted with a silicone seal in titanium, nickel base alloy, stainless steel or synthetic plastic material.

12. The pump of claim 9 wherein said reference electrode is a saturated calomel electrode.

13. The pump of claim 10 wherein said reference electrode is a saturated calomel electrode.

14. The pump of claim 1 wherein said counter electrode is platinized niobium on copper.

15. The pump of claim 1 wherein said counter electrode is 316L stainless steel.

16. The pump of claim 1 wherein said counter electrode is of U-bend form.

17. The pump of claim 1 wherein said counter electrode is of cantilever form with blow-out preventer.

18. The pump of claim 1 wherein said pump is provided with two coverplates, one on the suction side, the other on the pressure side.

19. The pump of claim 14 wherein said coverplate is of stainless steel, nickel base alloy or titanium.

20. The pump of claim 15 wherein said coverplate is of stainless steel, nickel base alloy or titanium.

21. The pump of claim 14 wherein said coverplate is of synthetic plastic material.

22. The pump of claim 14 wherein said coverplate is provided with a stainless steel backing plate.

23. The pump of claim 18 wherein said coverplates are situated on small side-arms set into the main process piping.

24. The pump of claim 18 wherein said side-arms are of the "T" or "Y" type.

WE CLAIM

The embodiments of the invention in which an exclusive property or privilege is claimed are defined as follows:

1. A pump for pumping an aqueous oxidizing chloride-ion-containing liquid or chemical pulping liquor, the pump comprising: (i) a stainless steel or carbon steel casing; (ii) an inlet limb connected to said stainless steel or carbon steel casing; (iii) an outlet limb connected to said stainless steel or carbon steel casing; (iv) means electrically connecting said stainless steel or carbon steel casing to a source of DC voltage, thereby to induce the stainless steel or carbon steel casing to act as an anode or a cathode, as required; (v) at least one reference electrode secured within at least one of said inlet limb and said outlet limb; (vi) at least one counter electrode secured within the same said limb selected from said inlet limb and said outlet limb; and (vii) control means for impressing a protection potential to said stainless steel or carbon steel casing at a predetermined voltage of -800 $mV_{Ag/AgCl}$ or more positive, said predetermined voltage being sufficient to draw the stainless steel or carbon steel casing into a passive corrosion zone.

2. The pump of claim 1 wherein said outlet limb is made of stainless steel and electrically isolated from the pump body.

3. The pump of claims 1 or 2 wherein said inlet limb is made of stainless steel and electrically isolated from the pump body.

4. The pump of claim 1 wherein said outlet limb is made of glass-fibre reinforced plastic.

5. The pump of claims 1 or 4 wherein said inlet limb is made of glass-fibre reinforced plastic.

6. The pump of claim 1 wherein said counter electrode and said reference electrode are each placed on the outlet limb.

7. The pump of claim 1 wherein said counter electrode and said reference electrode are each placed on the inlet limb.

8. The pump of claim 1 wherein said counter electrodes and said reference electrodes are placed on both the outlet limb and the inlet limb.

9. The pump of claim 1 wherein said reference electrode is of the screw-in type.

10. A method of protecting a pump having a stainless steel or carbon steel casing, an inlet limb and an outlet limb, comprising the steps of: electrically connecting said stainless steel or carbon steel casing to a source of DC voltage, thereby to induce the stainless steel or carbon steel casing to act either as a cathode or anode; securing at least one reference electrode within at least one of said inlet limb and said outlet limb; securing at least one counter electrode within the same limb selected from said inlet limb and said outlet limb; and impressing a protection potential to said stainless steel or carbon steel casing at a predetermined voltage of -800 $mV_{Ag/AgCl}$ or more positive, said predetermined voltage being sufficient to draw the stainless steel or carbon steel casing into a passive corrosion zone but, where possible, not being sufficiently low to draw said stainless steel or carbon steel casing into a zone of uniform corrosion.

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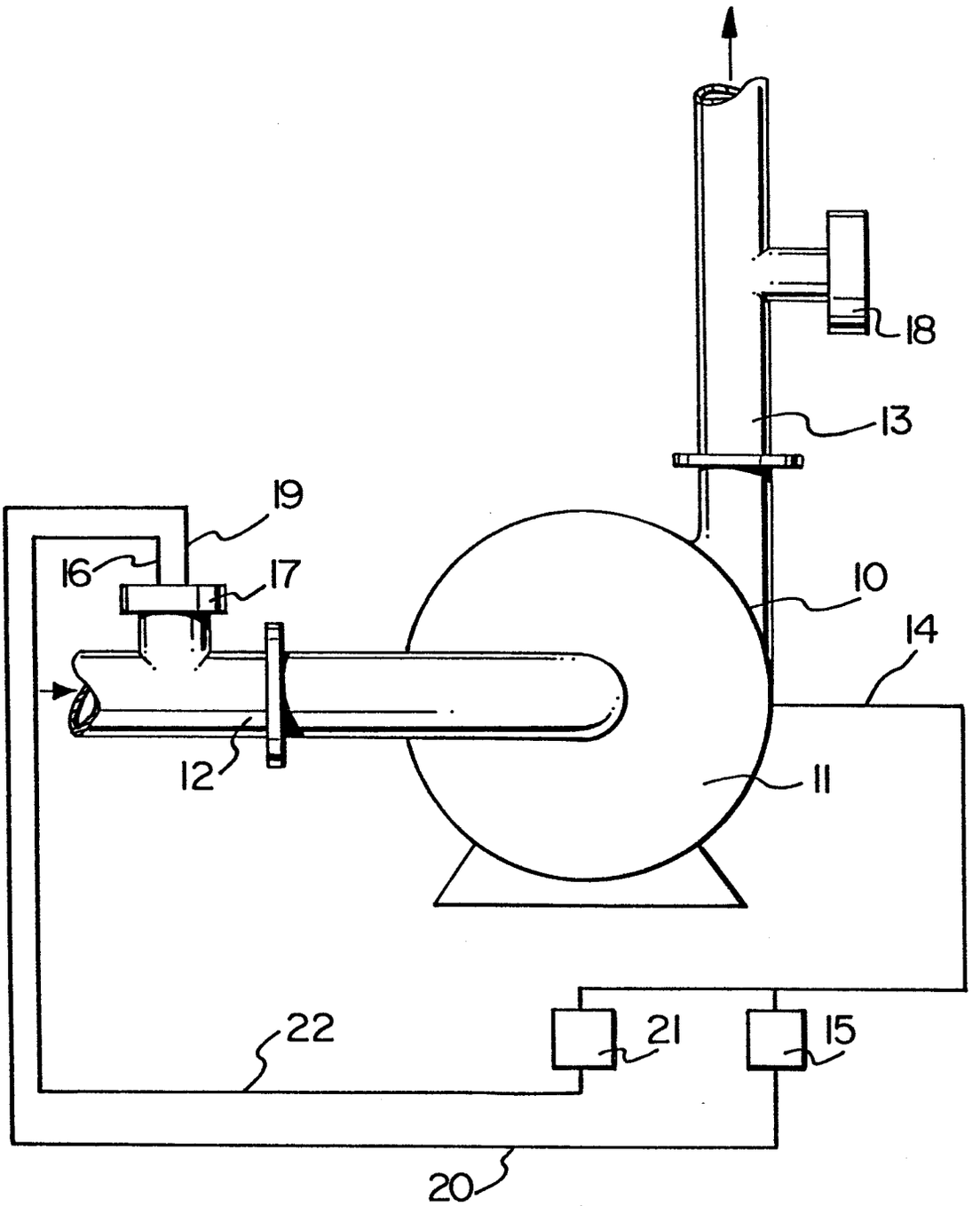

European Patent Office

EUROPEAN SEARCH REPORT

0142219
Application number

EP 84305346.3

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 4)
A	DD - A - 42 284 (K. SCHMIDT) * Claims * --	1,25	C 23 F 13/00 C 23 F 13/02 // D 21 C 9/10
A	DE - B - 1 253 994 (KLEIN, SCHANZLIN & BECKER AKTIENGESELLSCHAFT) * Claims * ----	1,25	D 21 C 3/22

TECHNICAL FIELDS SEARCHED (Int. Cl.4)

B 23 F
D 21 C

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
VIENNA	23-11-1984	SLAMA

CATEGORY OF CITED DOCUMENTS

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

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

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