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(54) METHOD AND DEVICE FOR CONTINUOUS ELECTROLYTIC DISPOSAL OF WASTE WATER

(76) Inventor: **Ryushin Omasa**, Kanagawa (JP)

Correspondence Address:
Frommer Lawrence & Haug
745 Fifth Avenue
New York, NY 10151 (US)

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(57) **ABSTRACT**

An apparatus for continuously electrolyzing waste liquid has a series (**10**) of tanks comprising a plurality of electrolytic tanks each having an anode (**22**) and a cathode (**23**), the electrolytic tanks being connected in series, vibrating flow generating means (**16**) which is equipped to each of the electrolytic tanks and generates vibrating flow in waste liquid (**14**) to be treated, and a power supply circuit (**34**) for applying a voltage between the anode (**22**) and the cathode (**23**). The vibrating flow generating means (**16**) has a vibration motor (**16*d***), vibration transmitting rods (**16*e***) which are operationally connected to the vibration motor (**16*d***) so as to vibrate in the waste liquid (**14**) to be treated; and vibrating vanes (**16*f***) fixed to the vibration transmitting rods (**16*e***). The distance between the anode (**22**) and the cathode (**23**) is equal to 5 to 50 mm. Vibrating stress dispersing means is interposed between the vibration motor (**16*d***) and the vibration transmitting rods (**16*e***) and/or between the vibration transmitting rods (**16*e***) and the vibrating vanes (**16*f***). The vibration motor (**16*d***) is commonly used by plural vibrating flow generating means. Plural electrolytic tanks constituting the series (**10**) of tanks are unified, and the electrolytic tanks thus unified are partitioned by partition walls (**11**).

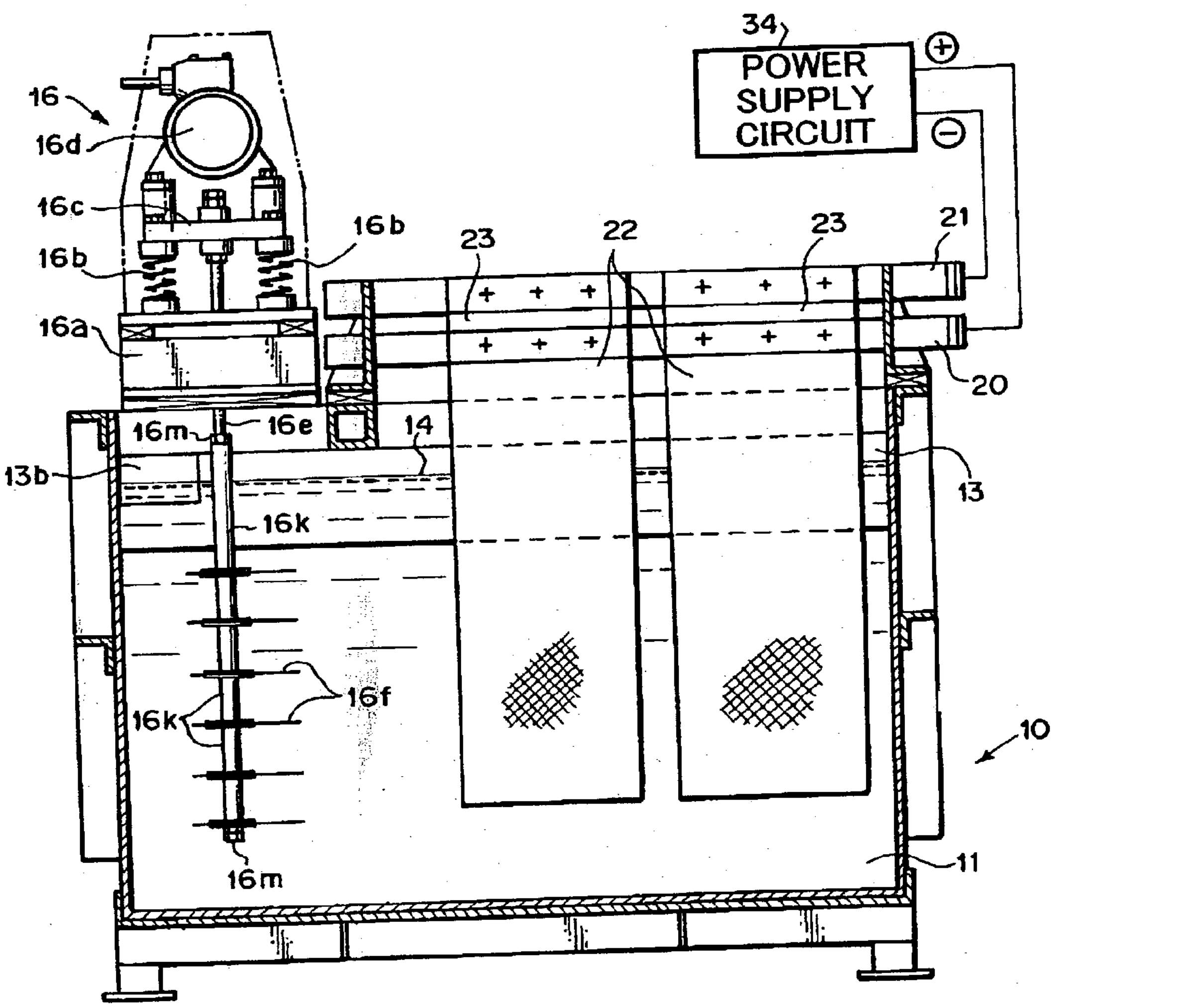
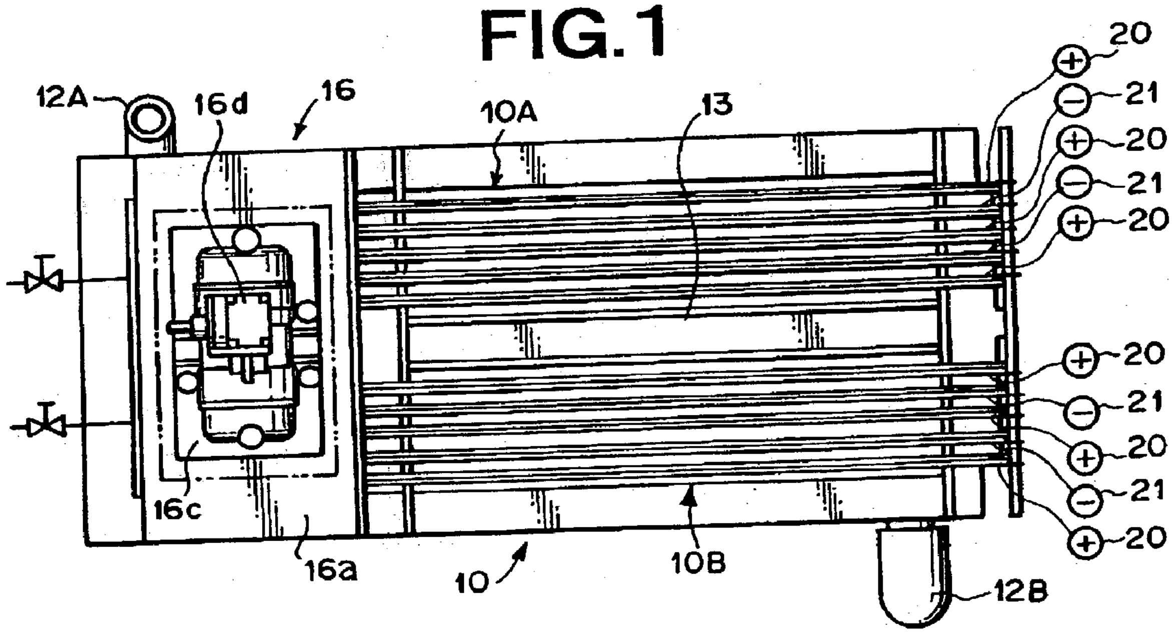


FIG.1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16d
16
10A
13
20
21
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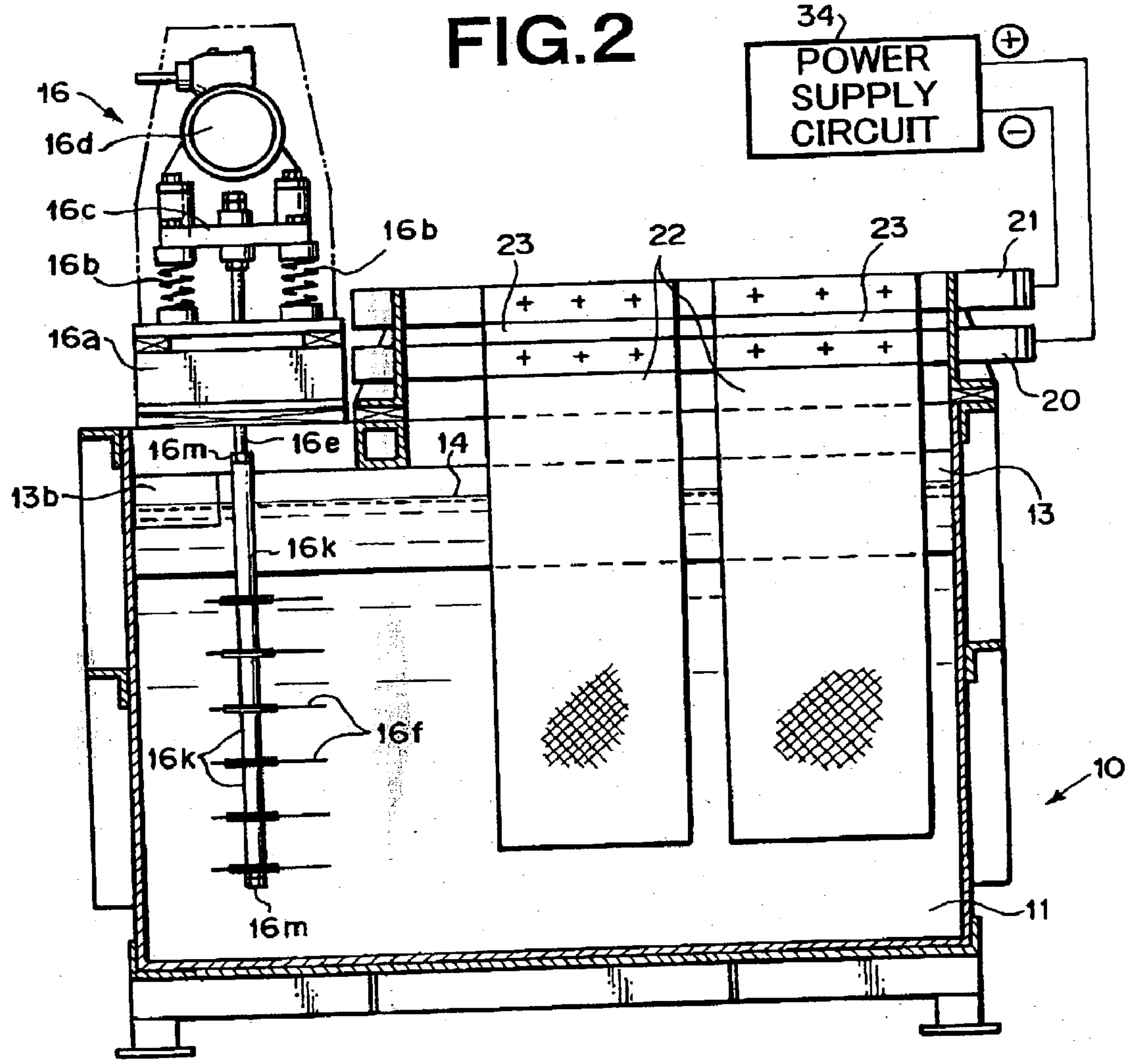
21
20
20
21
20
21
20
16c
16a
10
10B
12B

FIG.2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POWER SUPPLY CIRCUIT
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16d
16c
16b
16b
16a
23
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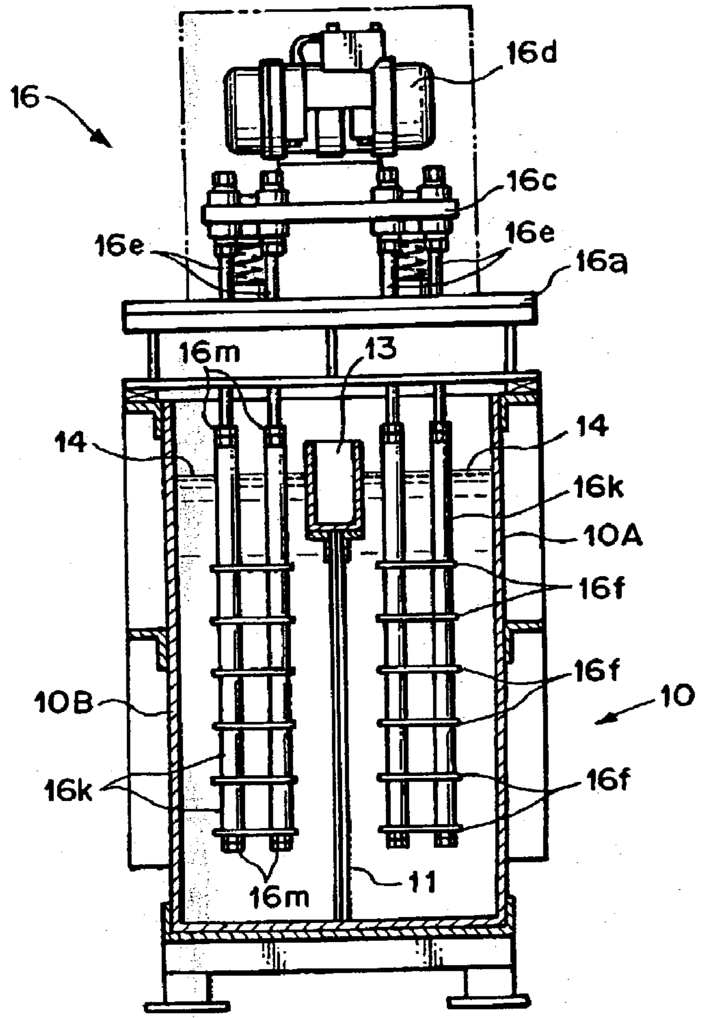
21
20
16m
16e
14
13b
16k
13
16f
16k
10
16m
11

FIG.3



16
16d
16c
16e
16e
16a
16m
13
14
14
16k
10A
16f
16f
10B
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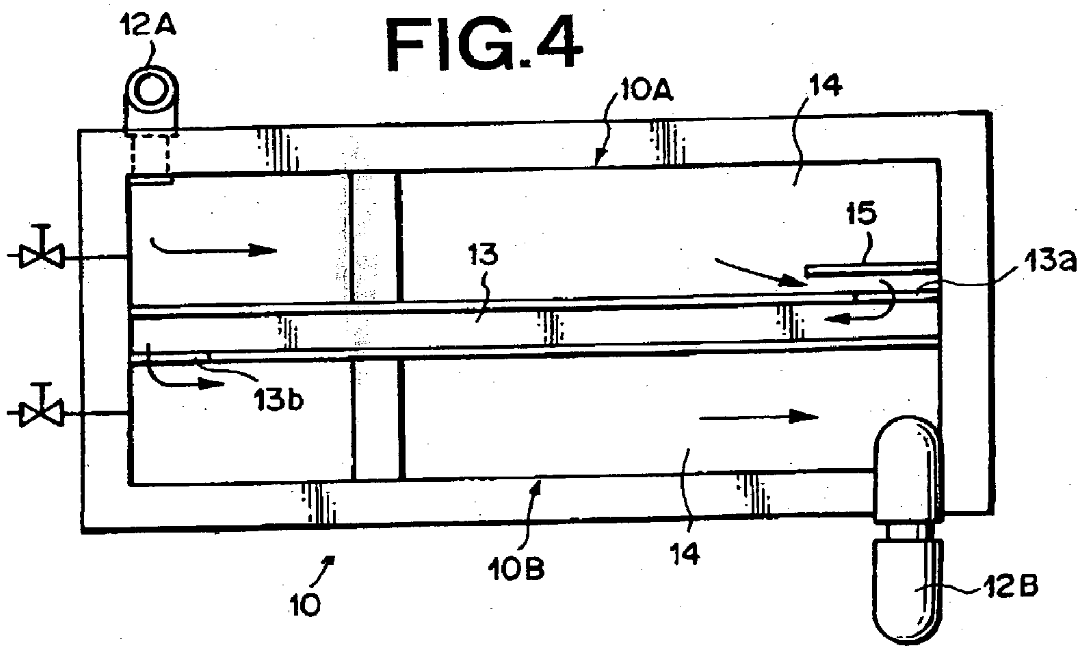
16k
16f
16m
11

FIG.4



12A
10A
14
15
13
13a
13b
10
10B
14
12B

FIG.5

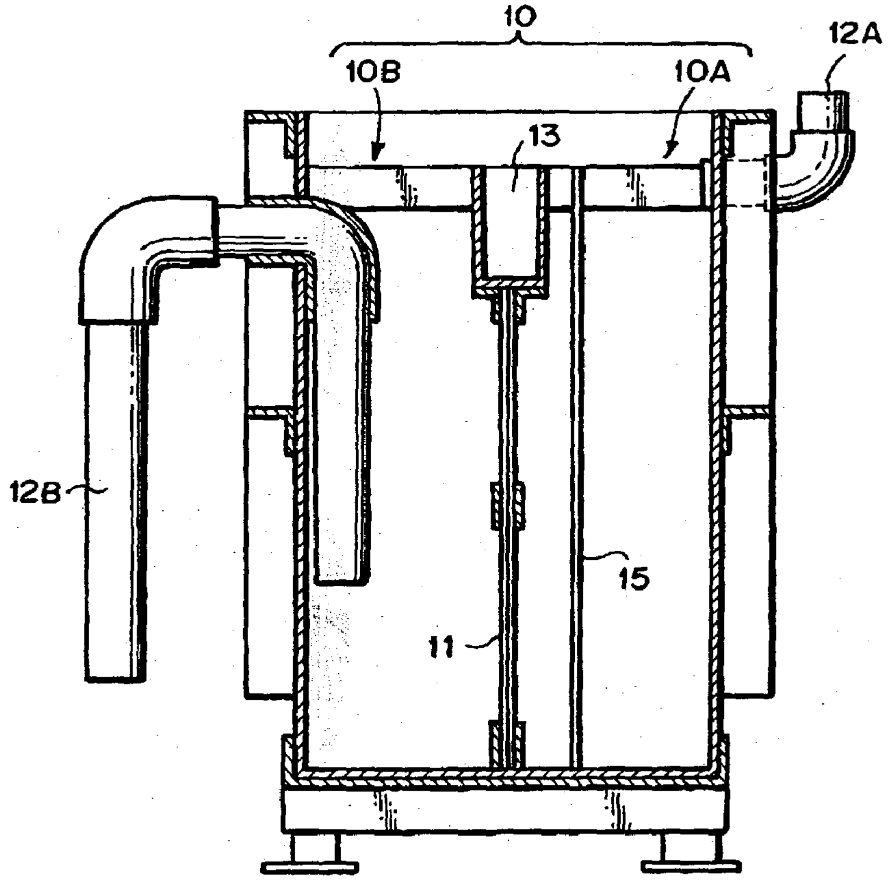


FIG.6

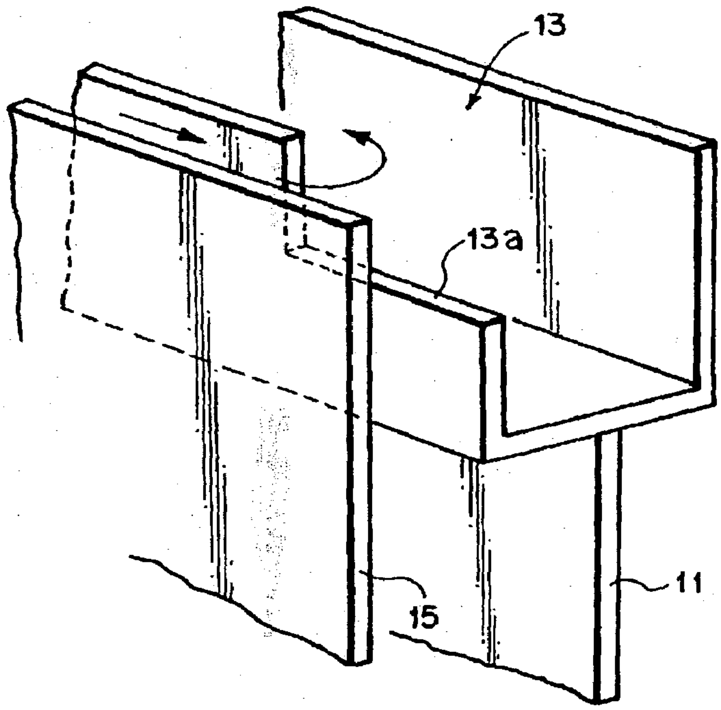


FIG. 7

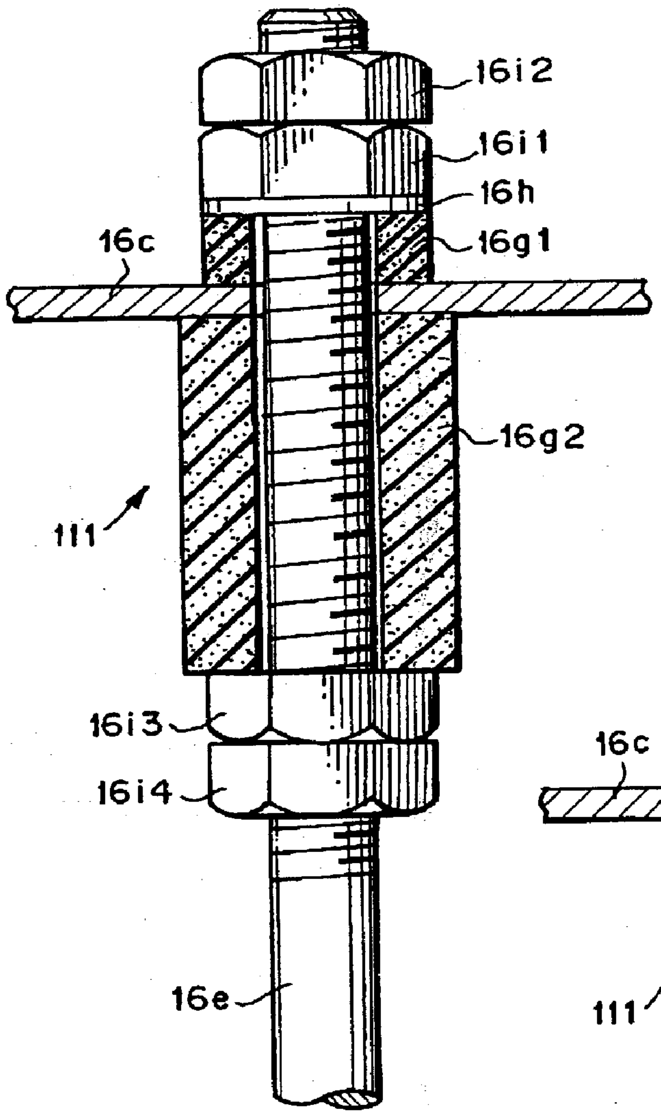
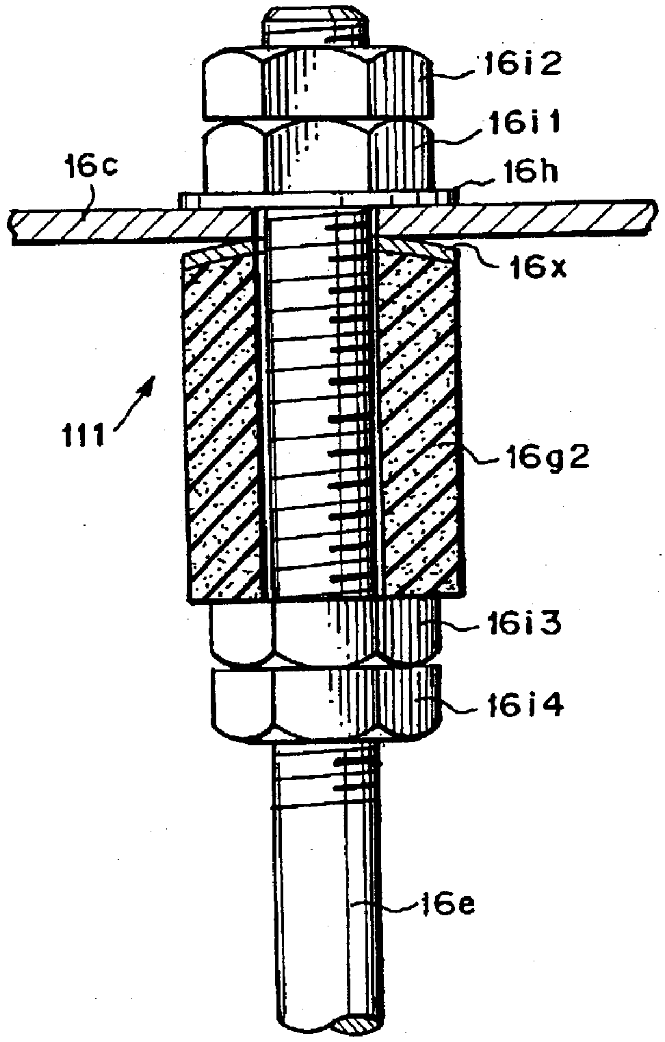

16i2
16i1
16h
16c
16g1
16g2
111
16i3
16i4
16e

FIG. 8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16c
16h
16x
111
16g2
16i3
16i4
16e

FIG.9

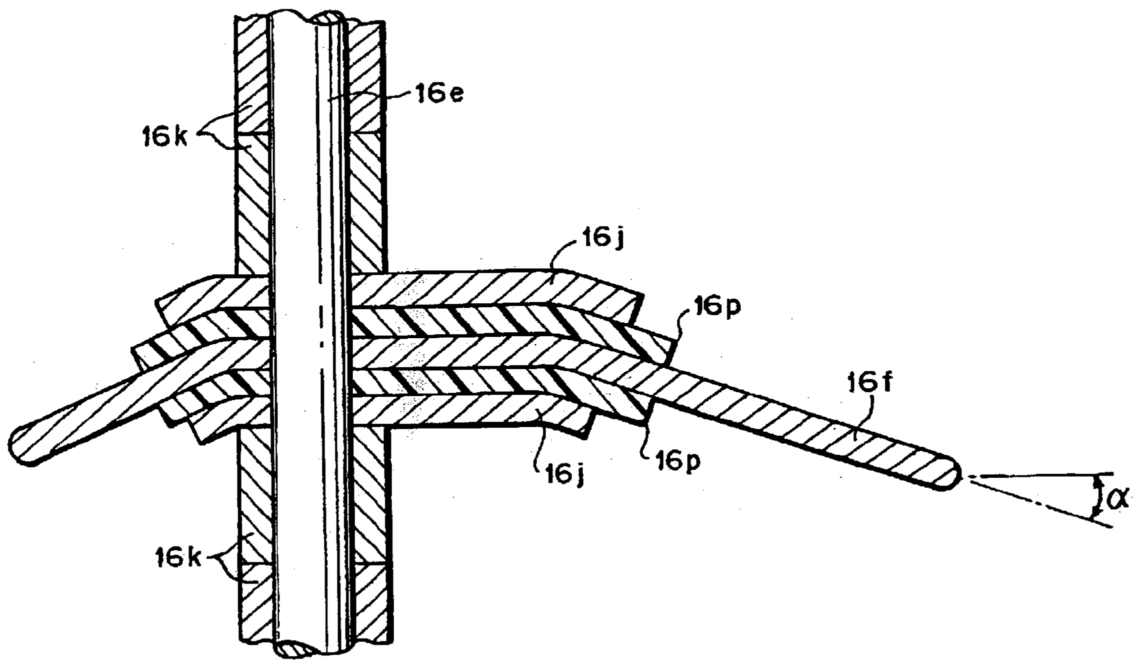


FIG.10

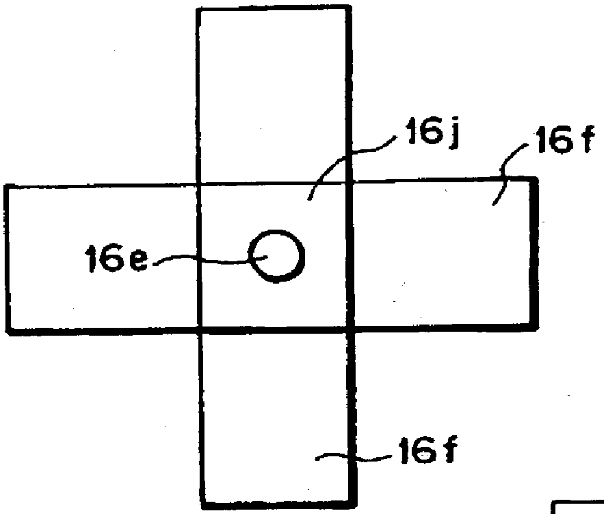


FIG.11

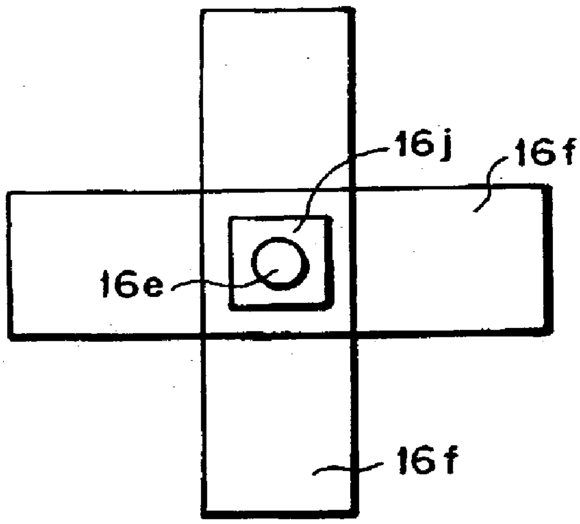


FIG.12

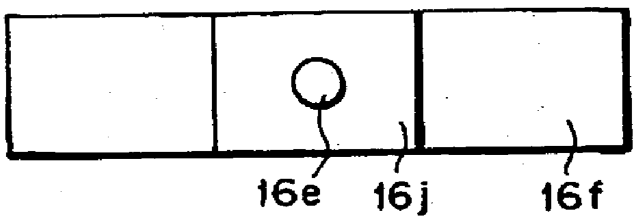


FIG.13

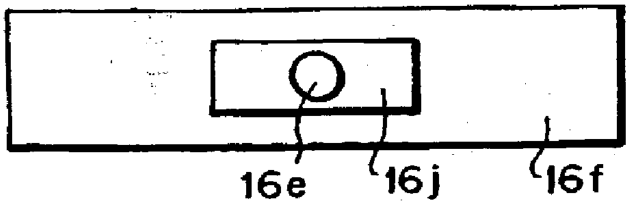


FIG. 14

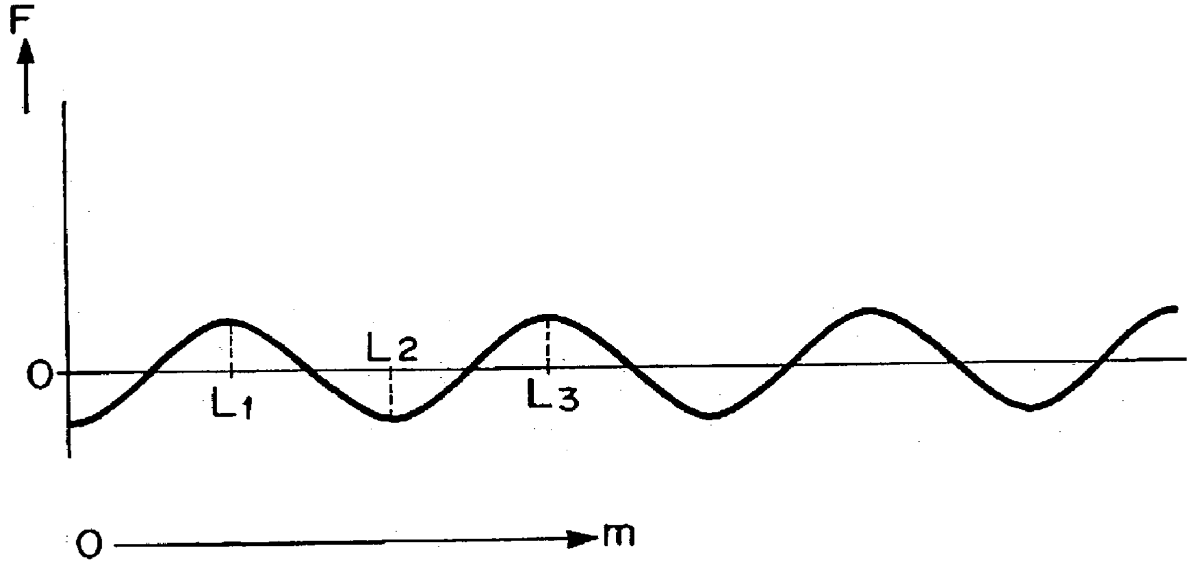


FIG.15

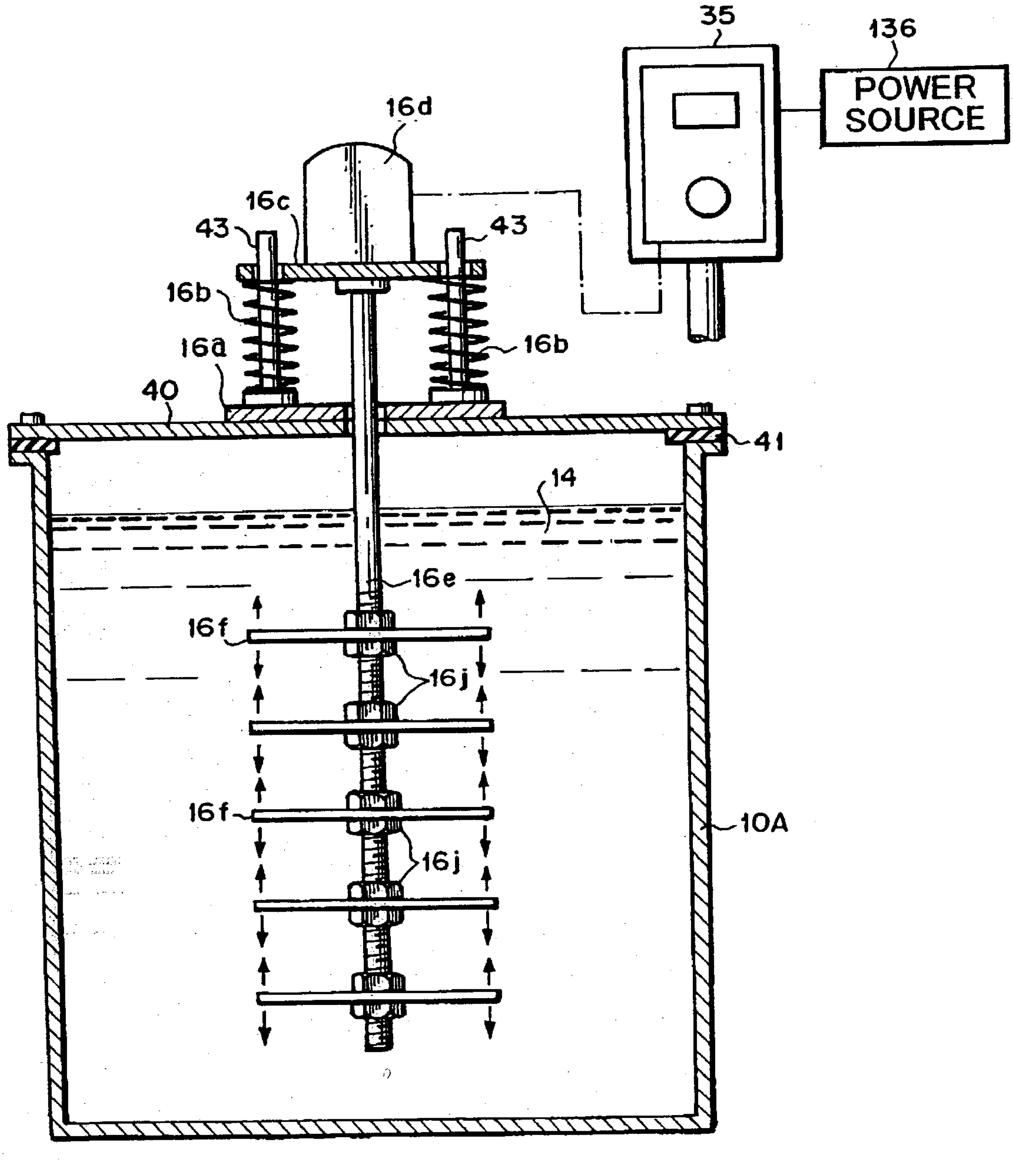

35
136
POWER SOURCE
16d
16c
43
43
16b
16b
16a
40
41
14
16e
16f
16j
16f
16j
10A

FIG. 16

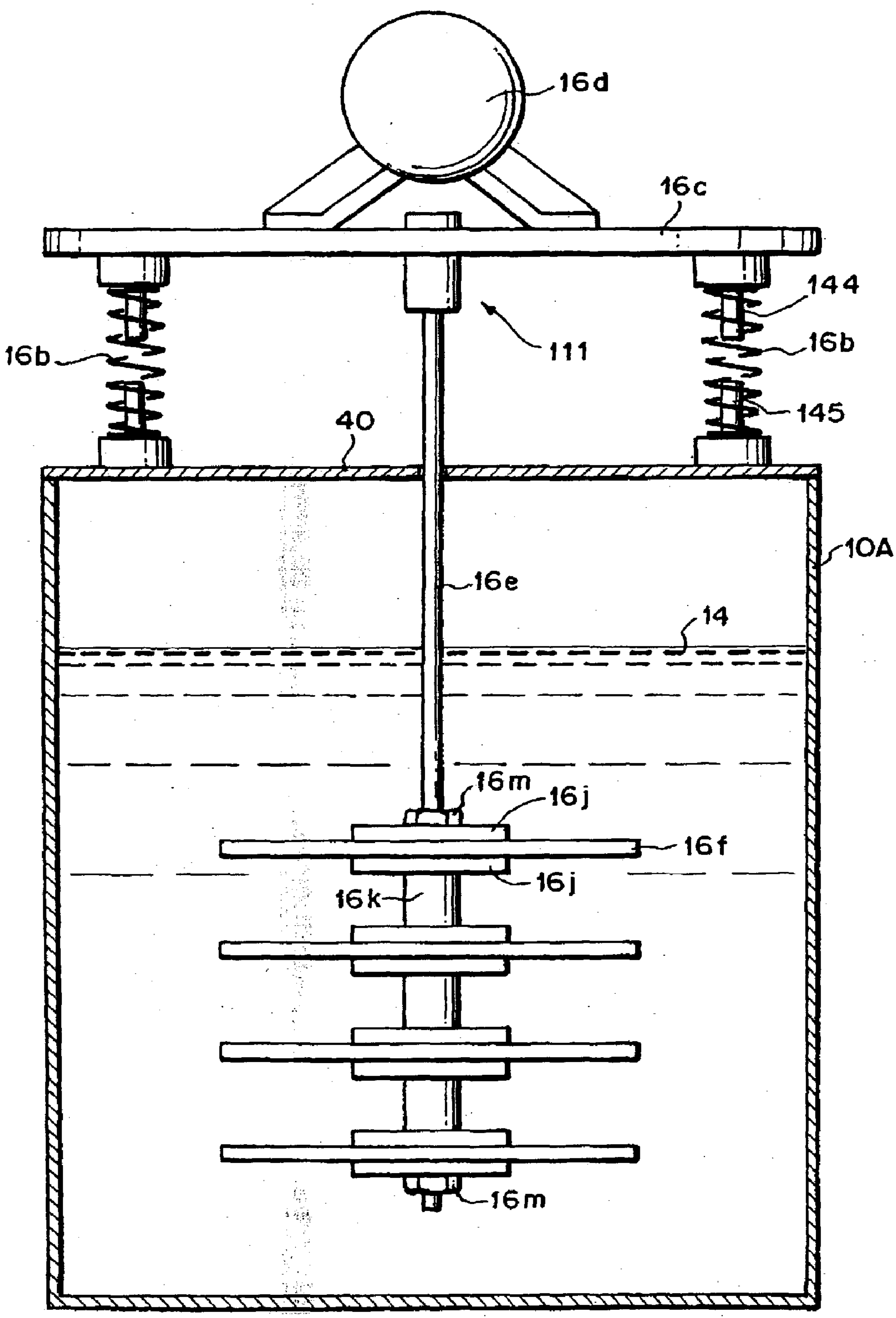


FIG. 17

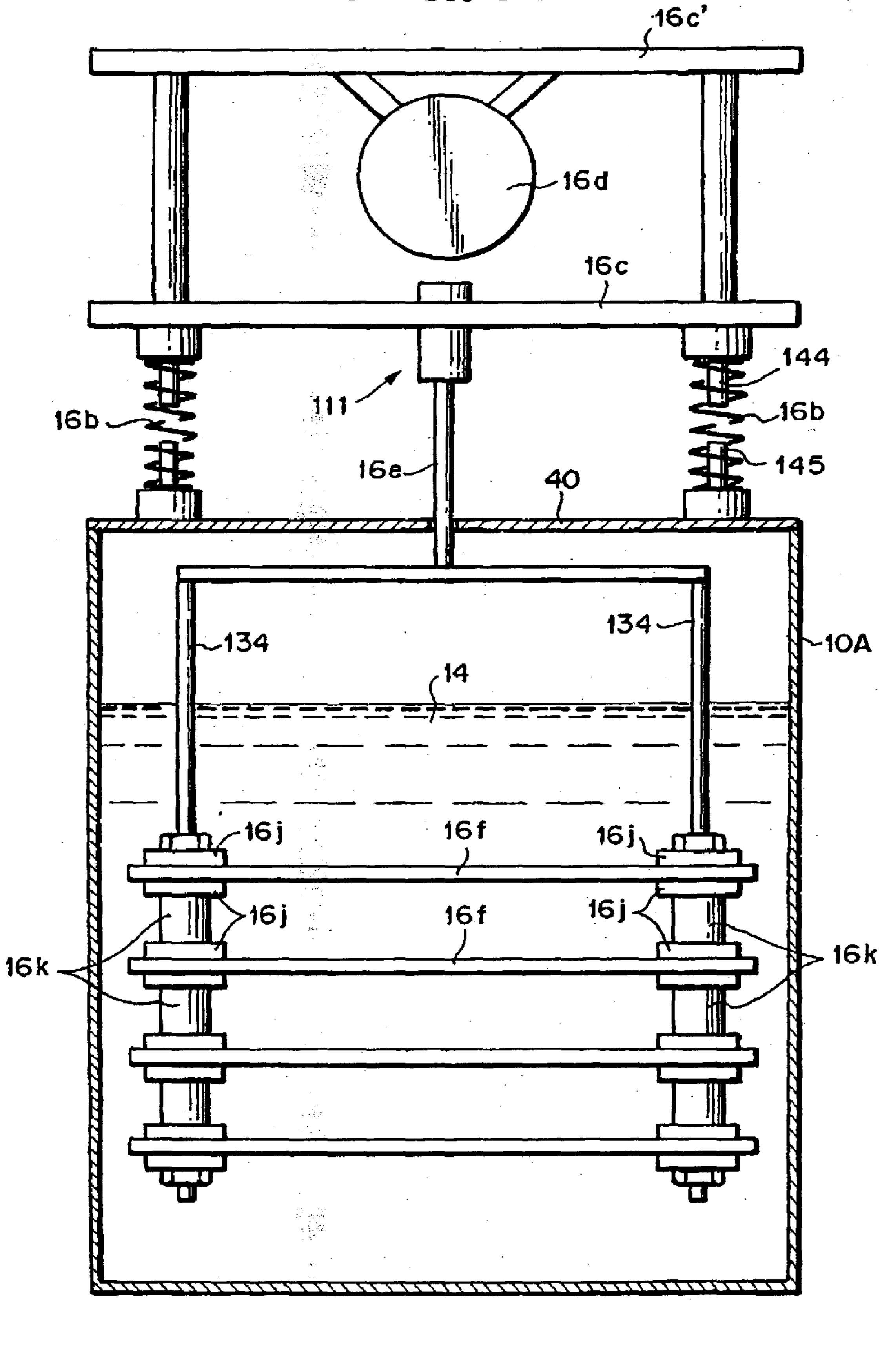

16c'
16d
16c
144
111
16b
16b
16e
145
40
134
134
10A
14
16j
16f
16j
16j
16f
16j
16k
16k

FIG. 18

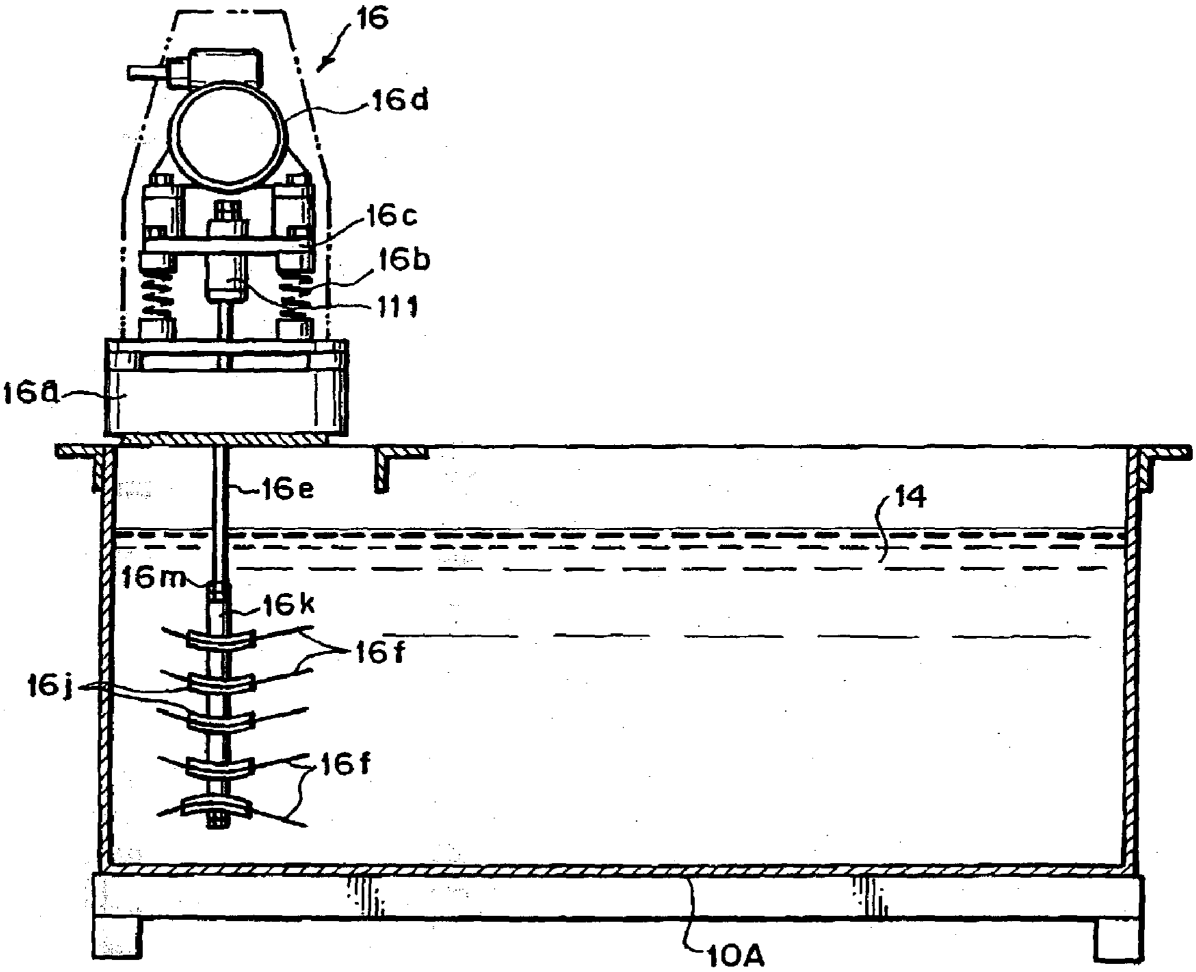


FIG. 19

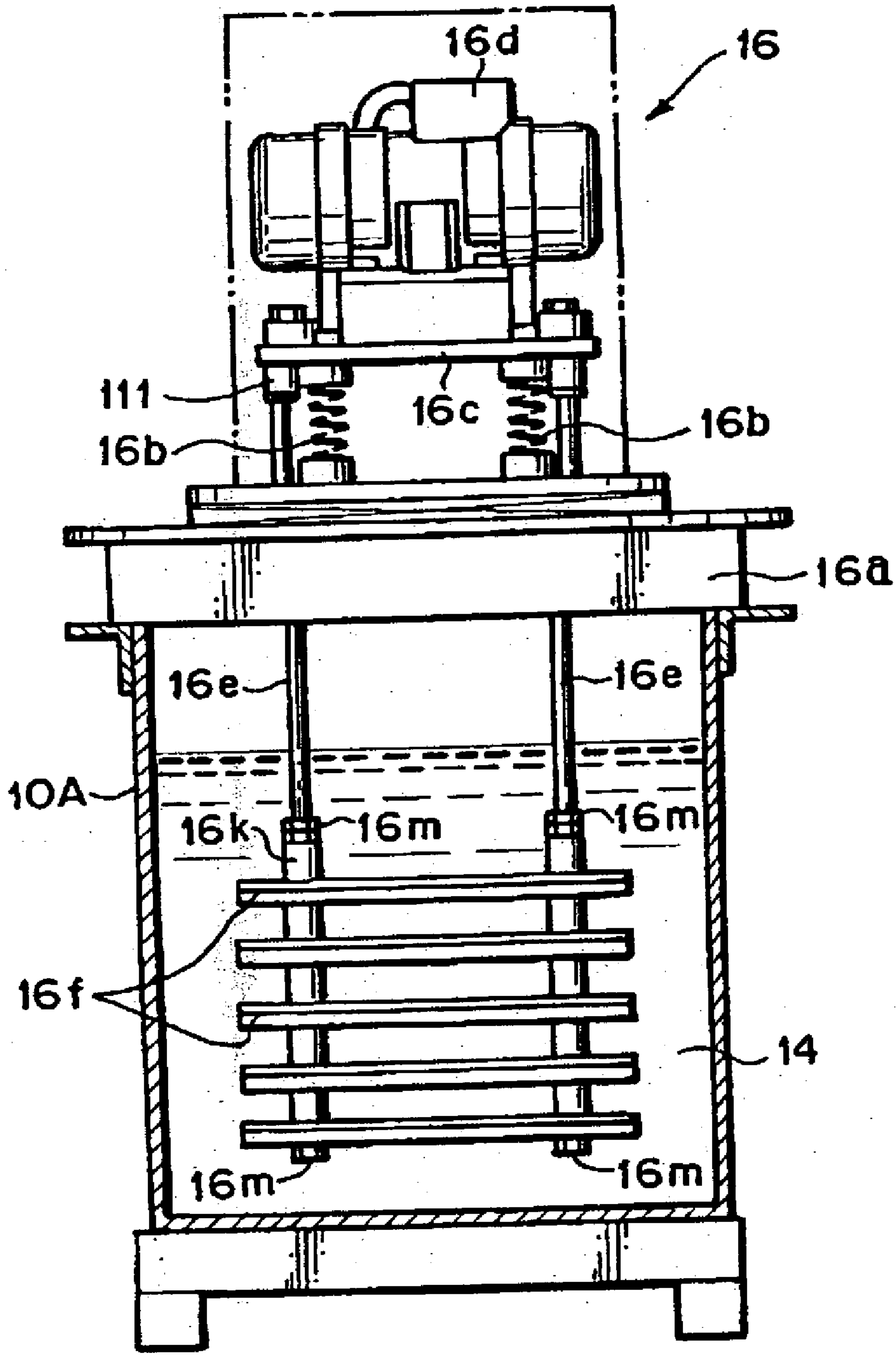


FIG.20

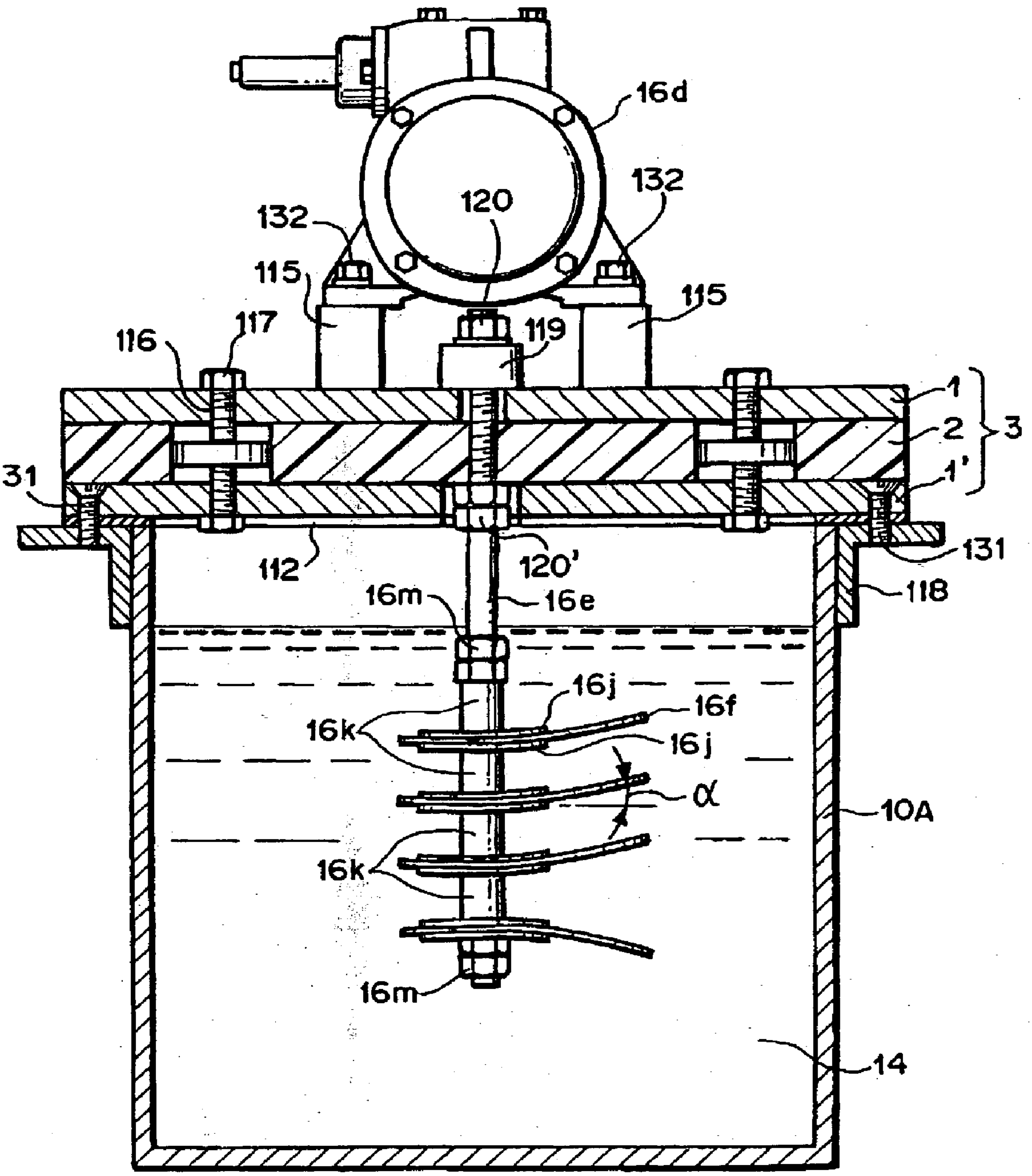

16d
132
120
132
115
115
117
116
119
1
2
3
1'
131
131
112
120'
118
16m
16e
16j
16f
16k
16j
α
10A
16k
16m
14

FIG.21

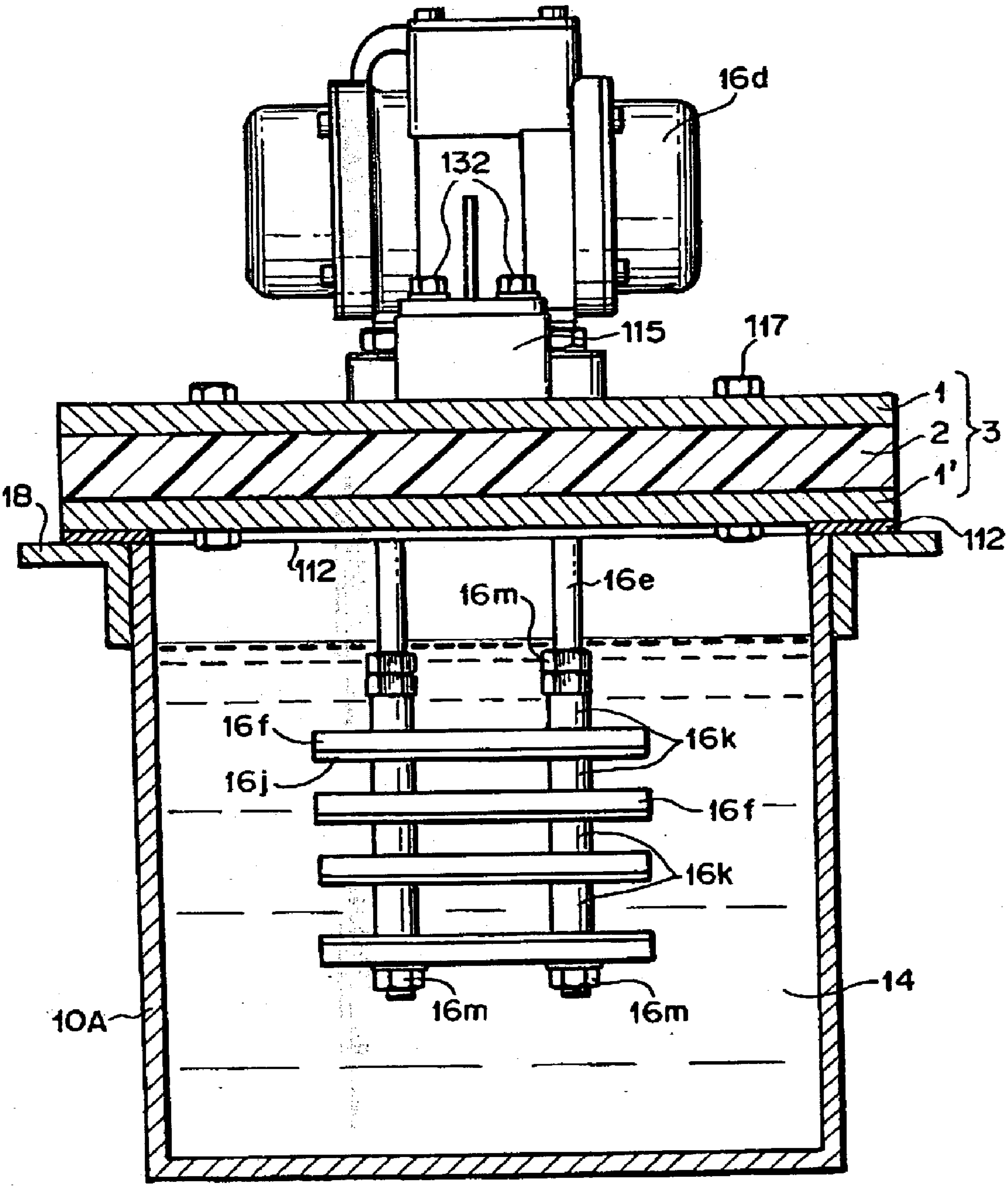

16d
132
115
117
1
2
3
1'
118
112
112
16m
16e
16f
16k
16j
16f
16k
14
10A
16m
16m

FIG.22

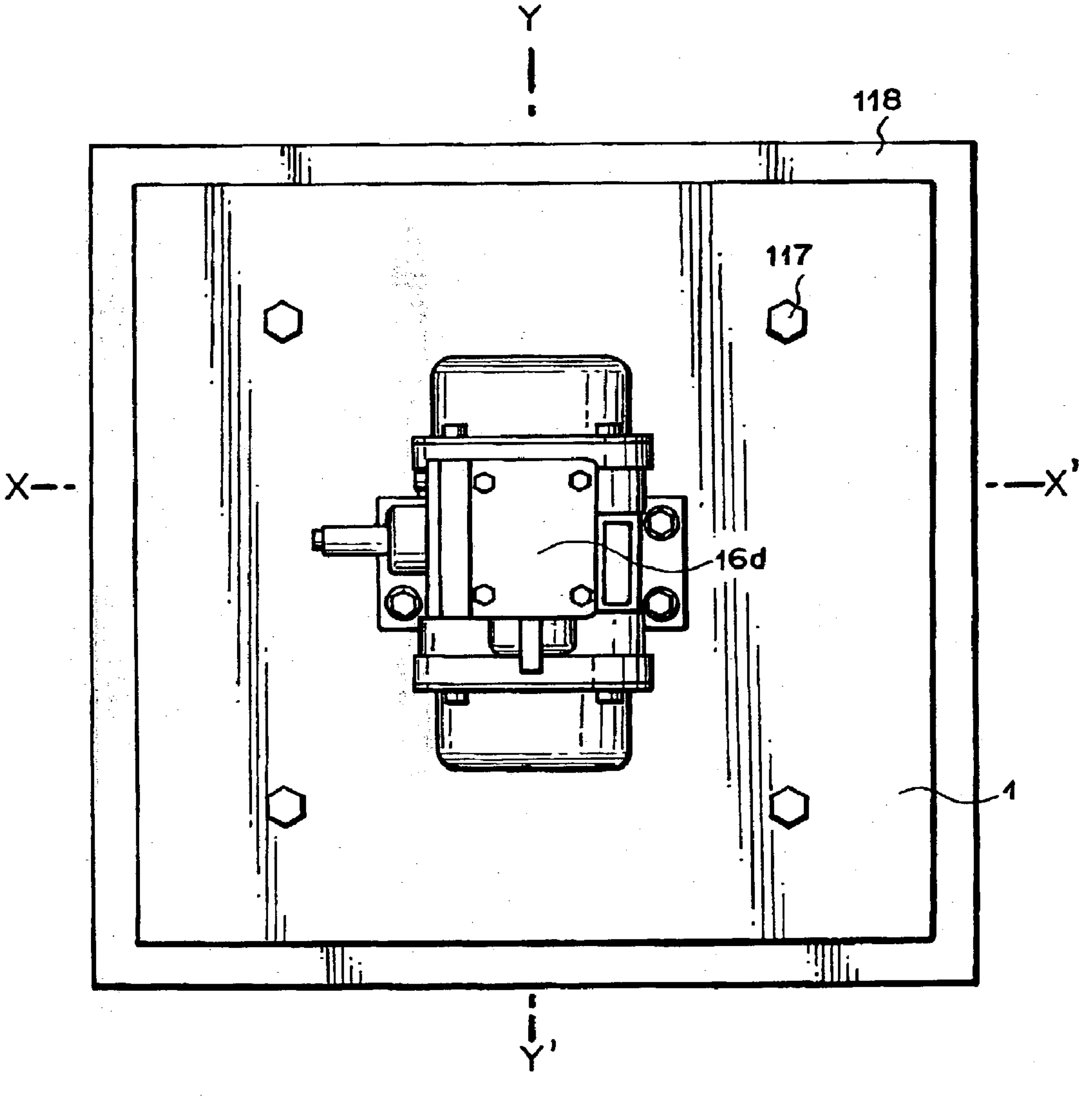


FIG.23A

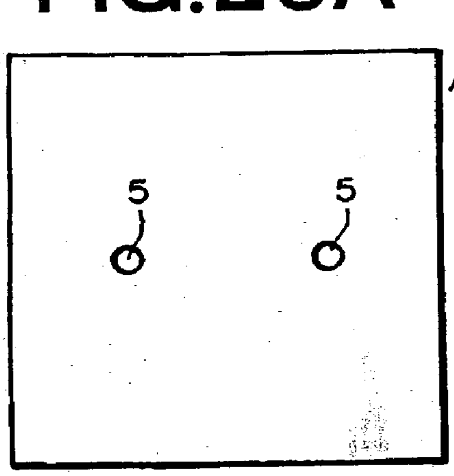


FIG.23B

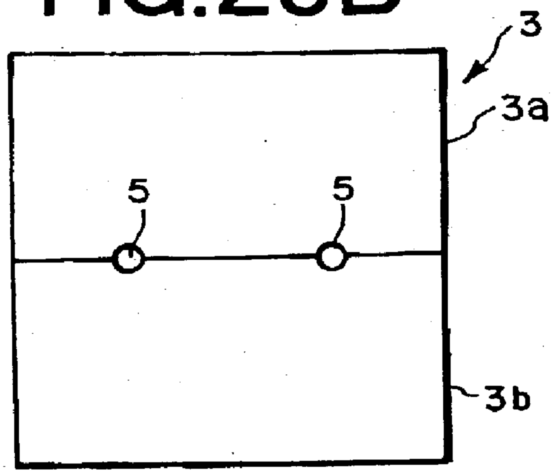


FIG.23C

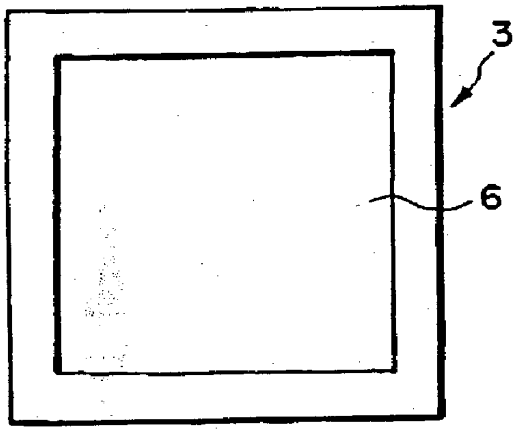


FIG.24A

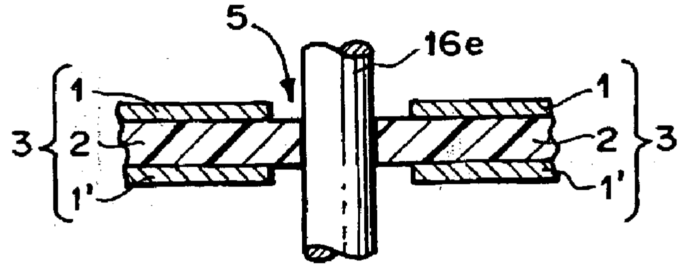


FIG.24B

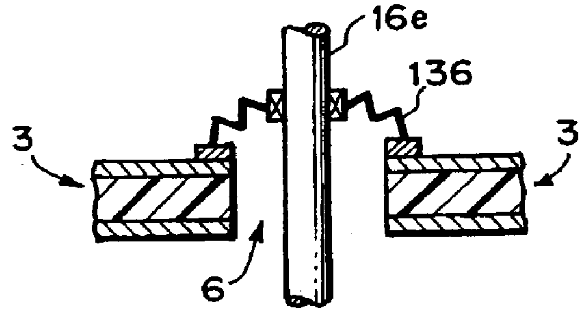


FIG.25A

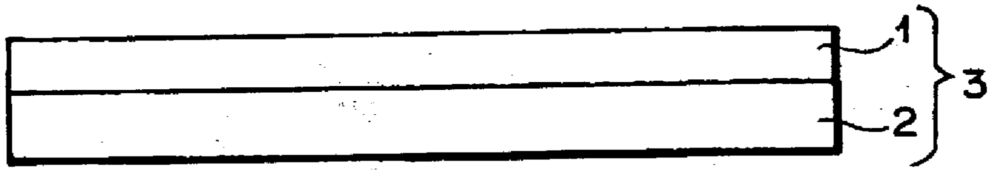


FIG.25B

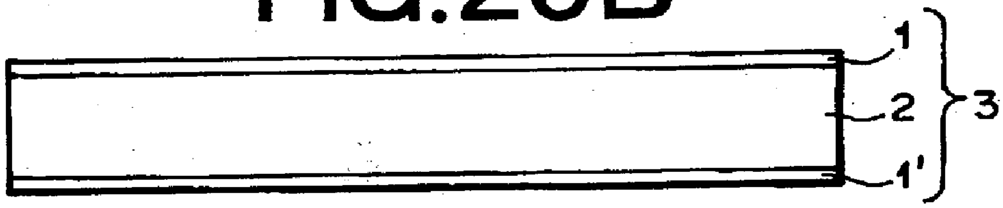


FIG.25C

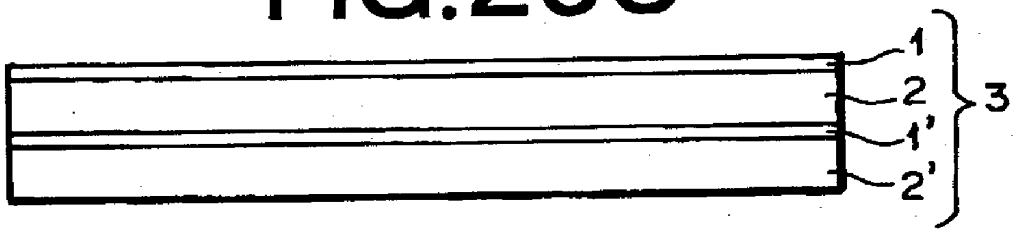


FIG.25D

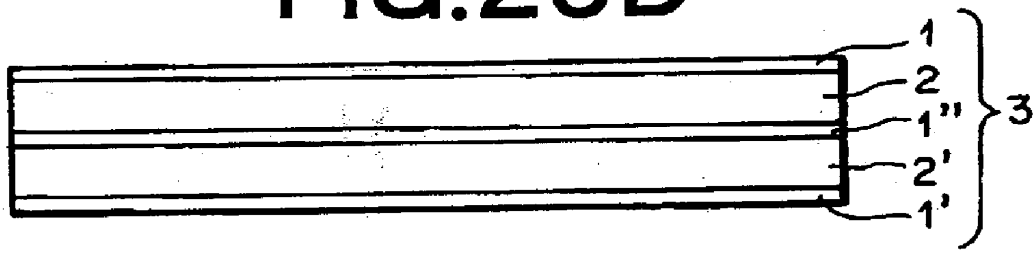


FIG.25E

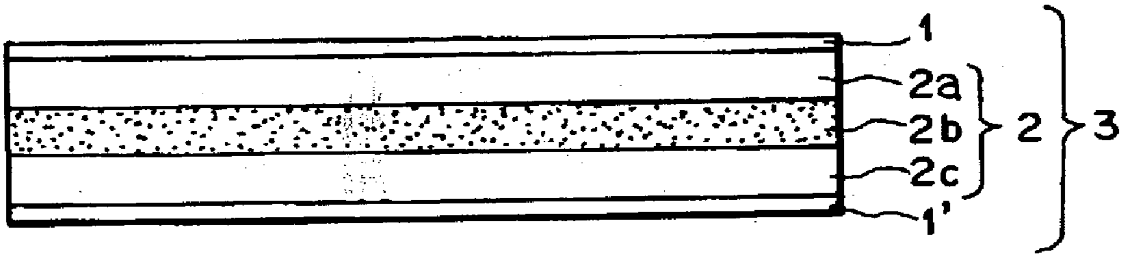
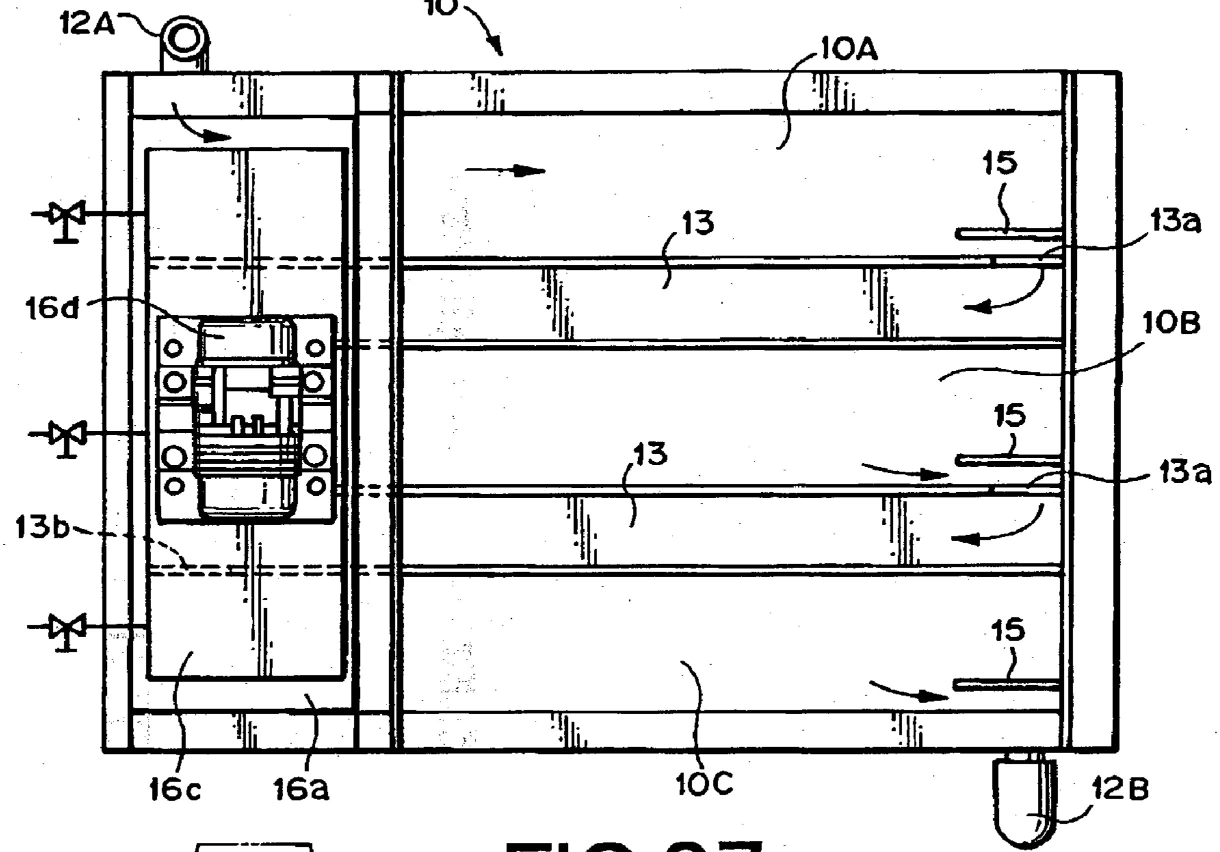
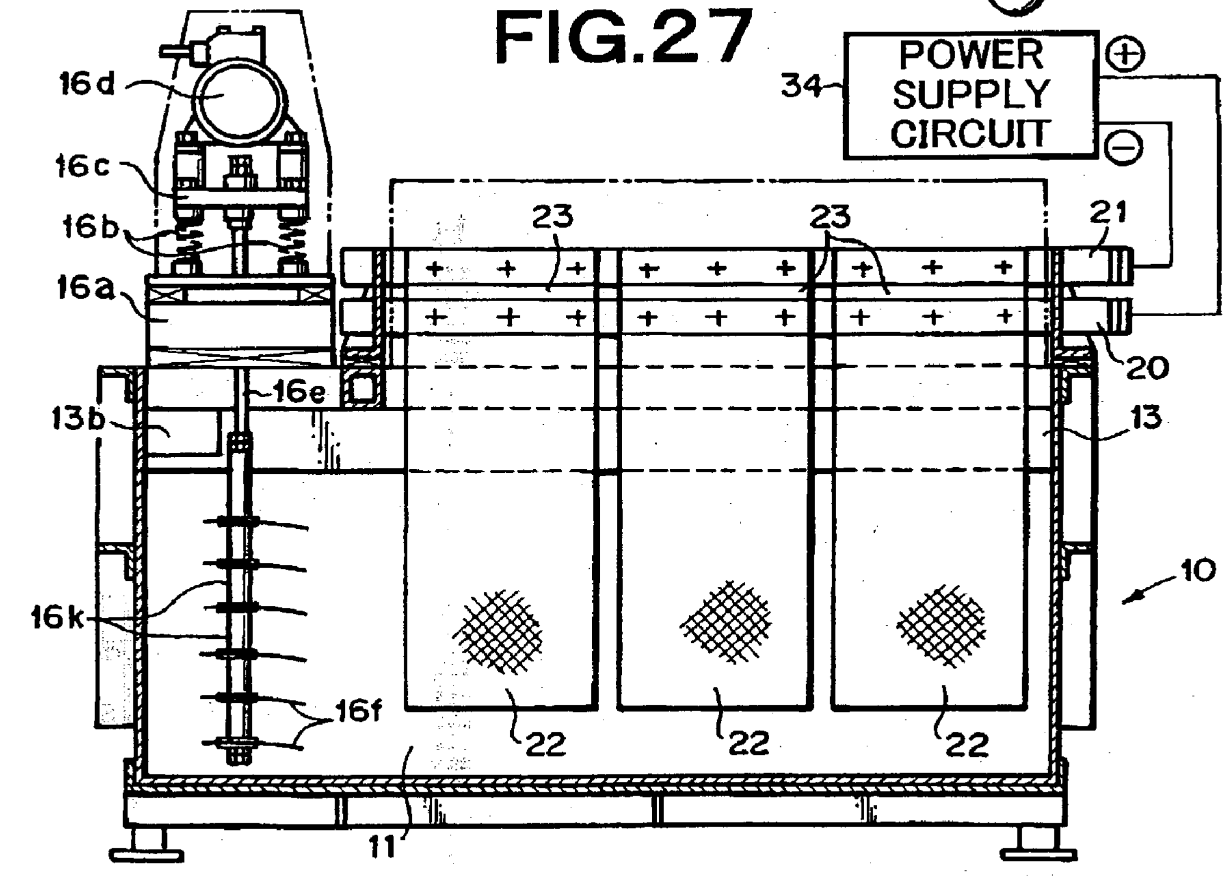


FIG.26



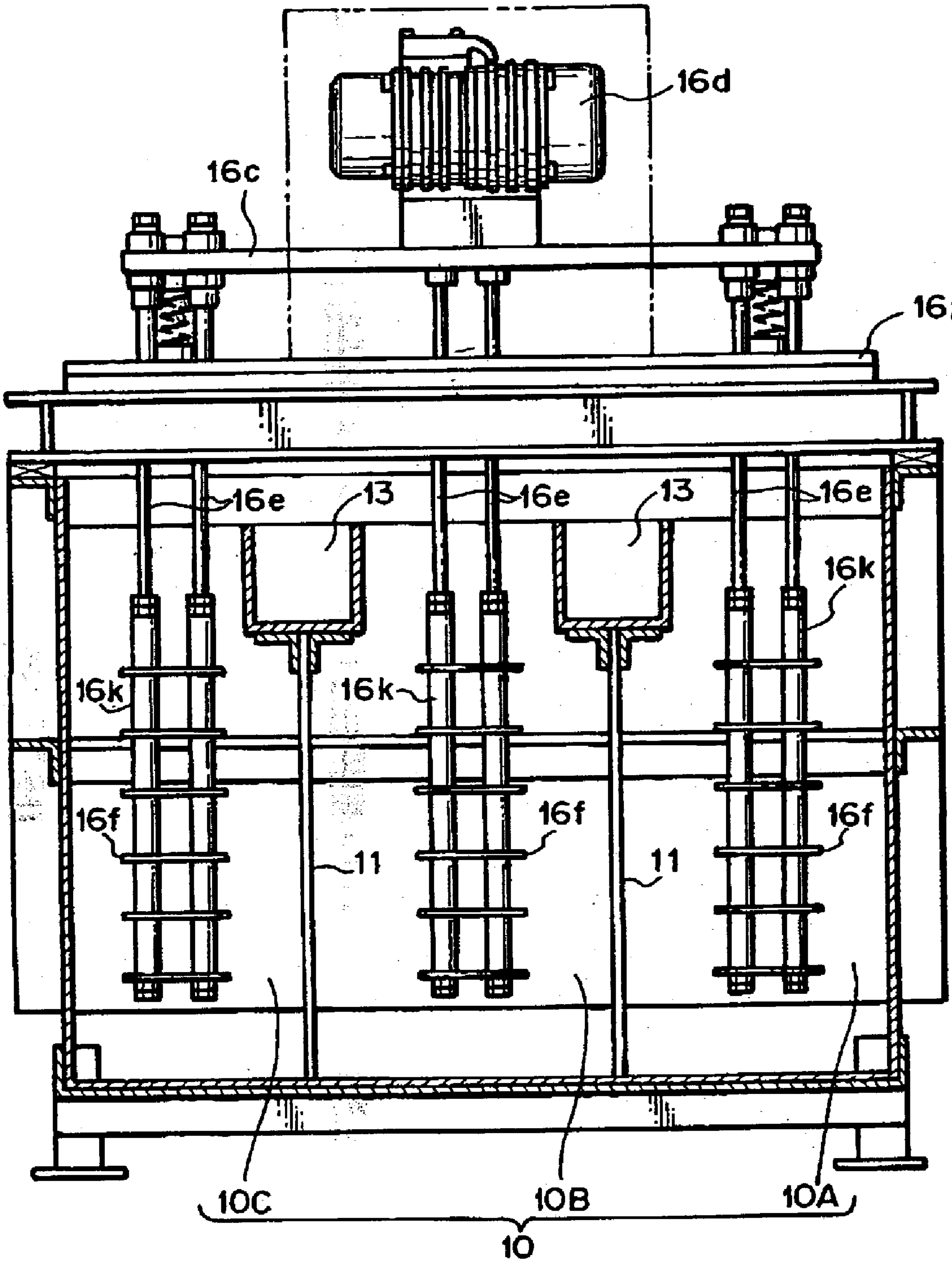
10
12A
10A
15
13
13a
16d
10B
15
13
13a
13b
15
16c
16a
10C
12B

FIG.27



16d
34
POWER SUPPLY CIRCUIT
16c
16b
23
23
21
16a
20
16e
13b
13
10
16k
16f
22
22
22
11

FIG.28


16d
16c
16a
16e
13
16e
13
16e
16k
16k
16k
16f
16f
16f
11
11
10C
10B
10A
10

METHOD AND DEVICE FOR CONTINUOUS ELECTROLYTIC DISPOSAL OF WASTE WATER

FIELD OF THE INVENTION

[0001] The present invention relates to method and apparatus for electrolyzing waste liquid continuously, and particularly to method and apparatus for continuously electrolyzing waste liquid containing metals at high speed.

BACKGROUND ART

[0002] Chromic acid exists in the form of anions such as CrO_4^{2-} or $Cr_2O_7^{2-}$ in plating solution used in a chrome plating treatment. At this time, chrome is hexavalent and has an auburn-based color. When chrome becomes trivalent, it has a cyan-based color. In a treatment process for chrome acid contained in chrome plating waste liquid, the waste liquid is acidified (pH 3.5 or less) by using sulfuric acid (chrome acid becomes bichromate ions in acidic solution of chrome acid), then hexavalent chromium in the waste liquid is reduced to trivalent chromium by using reducing agent, and then the waste liquid is neutralized into pH 7 to 8 in a neutralizing tank by pouring alkali into the waste liquid. Here, trivalent reduced chromium is precipitated as chromium hydroxide, the precipitants are removed as sludge, and then only clear supernatant liquid is discharged. The reduction potential of chromic acid is set to 250 mV (ORP meter) or less.

[0003] In order to conduct the reducing reaction efficiently, it is necessary to keep pH at 3 or less, and further as the reducing agent is used sodium bisulfite ($NaHSO_3$), sodium thiosulfate (NaS_2O_2, sodium hyposulfite), sulfur dioxide (SO_2), ferrous sulfate ($FeSO_4$), sodium sulfite (Na_2SO_3, sulfite of soda), sodium metabisulfite ($Na_2S_2O_2$) or the like. Comparing the priorities among these reducing agents, ferrous sulfate is preferable from the viewpoint of cost. However, when ferrous sulfate is used, it has a disadvantage that the amount of ferrous sulfate to be consumed is needed to be large, so that the amount of sludge occurring is increased. Further, when ferrous sulfate is used, ferrous ions are oxidized by chromium into auburn ferric ions. Therefore, the pollution caused by the ferric ions must be removed in order to enhance the water quality of the waste liquid. When sulfur dioxide is used as reducing agent, the reducing efficiency is high, however, pH and reducing conditions are severe. Therefore, if these conditions are deviated from predetermined ranges, it acts as acid rather than reducing agent and thus the reducing reaction does not progress. When the reducing reaction does not progress, excessive additives are discharged in the form of sulfur dioxide into the atmosphere, which causes air pollution. When sodium sulfite is used as reducing agent, it is preferable from the viewpoint that the solubility of sodium sulfite is high and the amount of sludge generated is relatively small. However, sodium bisulfite is generally broadly used from the viewpoint of the sludge generation amount, the price, the treatment, etc. With respect to the reduction of chromium, the reaction velocity is dependent on the pH value, and thus the reaction is carried out under the pH condition of 3.5 or less. If pH is larger than this value, the reaction velocity is lowered.

[0004] For reference, the amount of reducing agent required to treat chromic anhydride of 1 kg is shown in the following Table 1, and the amount of sludge generated due to addition of neutralizing agent in the treatment of chromic anhydride of 1 kg is shown in the following Table 2.

TABLE 1

REDUCING AGENT	AMOUNT FOR TREATMENT OF CHROMICANHYDRIDE OF 1 KG
Sodium bisulfite	1.6 kg to 3 kg
Sodium thiosulfate	7 kg
Sulfur dioxide	1.0 kg to 1.8 kg
Ferrous sulfate	8 kg to 16 kg
Sodium sullite	1.9 kg

[0005]

TABLE 2

REDUCING AGENT	NEUTRALIZING AGENT	SLUDGE AMOUNT
Sodium bisulfite	Quick lime	4.0 kg
Sodium bisulfite	Caustic soda	1.1 kg
Ferrous sulfate	Quick lime	12.0 kg
Ferrous sulfate	Caustic soda	4.2 kg

[0006] Little study has been hitherto made on the method of electrolytically treating waste liquid of chromic acid, and the number of practical examples is small. In addition, the conventional electrolyzing method is not proper to the treatment of dense solution, and it would be possible to apply this method to electrolytic reduction of solution only when the electrolytic reduction is carried out only in a batch process and also the solution is limited to ram solution such as washing water or the like. However, in the conventional electrolytic method, the distance between electrodes is set to 80 mm or more because there is a risk that explosion occurs if the distance between electrodes is small. Therefore, the time required for the treatment is long (three to five hours), and the continuous treatment is substantially impossible.

[0007] As an example of the treatment condition of the conventional electrolytic method, the electrolytic reaction is carried out under the condition of pH2 or less and the current density of 0.5 to $2A/dm^3$. However, the conventional electrolytic method has various problems under the actual practical operation, for example, breakdown of electrodes, increase of consumption power, unsuitableness to dense waste liquid, etc. Therefore, it is difficult to use this method under the present circumstances (see the section "ELECTROLYTIC REDUCTION TREATMENT" in the chromic acid treatment of "PLATING TECHNIQUE MANUAL").

[0008] In addition, the method of electrolytically treating chromic acid waste liquid by using chemicals has been broadly recognized as being environmentally very harmful at all times. Various treatment methods and alternative methods to solve these problems have been studied, however, there has not yet been discovered any low-cost treatment method in which not only the use amount of chemicals such as reducing agent descried above, etc. can be reduced, but also no chromium is discharged. The following is the present problems occurring in the method of electrolytically treating waste liquid of chromic acid by using chemicals:

[0009] (1) high running cost;

[0010] (2) occurrence of abnormal odor based on sulfide contained in reducing agent and its harmfulness;

[0011] (3) abnormal odor emitted from a treatment tank and its harmfulness;

[0012] (4) adverse effect of residual reducing agent on subsequent chemical treatment process (aggregation effect and precipitation effect are reduced); and

[0013] (5) outflow of hexavalent chromium caused by reduction in throughput capacity.

[0014] Further, the applicant of this application previously proposed a method and an apparatus for treating metal-contained waste liquid by electrolytic oxidation in Japanese Patent No. 2767771. However, in the technique disclosed in this publication, the reducing or oxidizing step itself based on electrolysis is carried out in the batch process. That is, with respect to the conventional electrolytic waste liquid treatment method, it has been estimated that it is impossible to continuously carrying out the reducing or oxidizing process itself because the practically sufficient treatment velocity cannot be achieved.

[0015] Further, it is general that plating factory waste liquid contains not only heavy metal, also sodium cyanide or potassium cyanide. These cyanides exist in the waste liquid while forming complex salts with heavy metals. The complex salts are very stable, and thus they cannot be removed by normal treatments. In addition, the density of cyanogen in plating waste liquid is equal to about 50,000 to 60,000 ppm, and under such a high density, cyanogen cannot be removed by normal chemical treatments.

[0016] A method of conducting the electrolytic treatment in combination with oxidizing agent is proposed as a method of withdrawing metals from waste liquid containing metals and cyanogen and also decomposing cyanogen (see JP(A)-9-225470). However, this method has various problems. For example, this method produces ammonia in the electrolytic reaction, and adversely affects the surrounding environment. Further, even when this method is applied to a case where the density of cyanogen is relatively low (for example, 1000 ppm or less), the treatment needs several hours or more and thus the treatment time is long.

[0017] An object of the present invention is to provide a method and an apparatus which needs neither reducing agent nor oxidizing agent as chemicals, and reduces metal ions in waste liquid by hydrogen occurring from one electrode to precipitate the metals while decomposing cyanogen into carbon dioxide and nitrogen by oxygen occurring form the other electrode, so that the metal components and/or cyanogen components can be removed highly efficiently and continuously in short time.

SUMMARY OF THE INVENTION

[0018] According to the present invention, in order to attain the above object, there is provided a method for continuously electrolyzing waste liquid, comprising the steps of:

[0019] continuously supplying waste liquid to be treated into a first electrolytic tank of series of tanks comprising a plurality number n (n represents an integer equal to or greater than 2) of electrolyte tanks each having an anode and a cathode, the electrolytic tanks being connected in series; and

[0020] continuously taking out treated waste liquid from an n-th electrolytic tank of the series of tanks,

[0021] wherein a voltage is applied between the anode and the cathode in each tank to electrolyze the waste liquid to be treated under the state that vibrating vanes fixed to vibrating rods which are operationally connected to vibration generating means so as to vibrate in the waste liquid to be treated are vibrated at an amplitude of 0.05 to 10.0 mm and at an oscillation frequency of 100 to 1500 cycles per minute to induce vibrating flow in the waste liquid to be treated.

[0022] In an aspect of the present invention, the vibrating flow is generated so that the three-dimensional flow velocity of the waste liquid to be treated is equal to 150 mm/second or more. In an aspect of the present invention, the vibration generating means is vibrated at a frequency of 10 to 500 Hz.

[0023] In an aspect of the present invention, the distance between the anode and the cathode is kept to be equal to 5 to 50 mm. In an aspect of the present invention, a voltage of 4 to 15V is applied between the anode and the cathode.

[0024] According to the present invention, in order to attain the above object, there is also provided an apparatus for continuously electrolyzing waste liquid, comprising:

[0025] a series of tanks comprising a plurality number n (n represents an integer equal to or greater than 2) of electrolytic tanks each having an anode and a cathode, the electrolytic a being connected in series;

[0026] vibrating flow generating means which is equipped to each of the electrolytic tanks and generates vibrating flow in waste liquid to be treated; and

[0027] a power supply circuit for applying a voltage between the anode and the cathode,

[0028] wherein the vibrating flow generating means comprises vibration generating means; vibration transmitting rods which are operationally connected to the vibration generating means so as to vibrate in the waste liquid to be treated; and vibrating vanes fixed to the vibration transmitting rods.

[0029] In an aspect of the present invention, the distance between the anode and the cathode is set to 5 to 50 mm.

[0030] In an aspect of the present invention, vibrating stress dispersing means is interposed between the vibration generating means and the vibration transmitting rods and/or between said vibration transmitting rods and the vibration vanes.

[0031] In an aspect of the present invention, the vibration generating means is used commonly by plural vibrating flow generating means.

[0032] In an aspect of the present invention, plural electrolytic tanks constituting the series of tanks are unified, and the electrolytic tanks thus unified are partitioned by respective partition walls. In an aspect of the present invention, a chute is equipped between the respective continuous electrolytic tanks thus unified so that the waste liquid to be treated is fed from one electrolytic tank to the other electrolytic tank. In an aspect of the present invention, the chute is equipped with a flow-in cut-out portion into which the waste liquid to be treated flows from the one electrolytic tank of the continuous electrolytic tanks of the unified electrolytic tanks, and a flow-out cut-out portion from which the waste liquid to be treated flows out to the other electrolytic tank of the continuous electrolytic tanks of the unified electrolytic tanks. In an aspect of the present invention, the one electrolytic tank of the continuous electrolytic tanks of the unified electrolytic tanks is equipped with a dam adjacently to the flow-in cut-out portion.

BRIEF DESCRIPTION OF THE DRAWINGS

[0033] **FIG. 1** is a plan view showing the construction of a continuously electrolyzing apparatus in which a waste liquid continuously electrolyzing method of the present invention is performed;

[0034] **FIG. 2** is a cross-sectional view showing the continuously electrolyzing apparatus of **FIG. 1**;

[0035] **FIG. 3** is a cross-sectional view showing the continuously electrolyzing apparatus of **FIG. 1**;

[0036] **FIG. 4** is a partially-omitted plan view showing the continuously electrolyzing apparatus of **FIG. 1**;

[0037] **FIG. 5** is a partially-omitted cross-sectional view showing the continuously electrolyzing apparatus of **FIG. 1**;

[0038] **FIG. 6** is a partially-omitted perspective view showing the neighborhood of a flow-in cut-out portion of the continuously electrolyzing apparatus of **FIG. 1**;

[0039] **FIG. 7** is an enlarged cross-sectional view of a fixing portion of a vibration transmitting rod to a vibration member of the continuously electrolyzing apparatus of **FIG. 1**;

[0040] **FIG. 8** is an enlarged cross-sectional view showing a modification of the fixing portion of the vibration transmitting rod to the vibration member;

[0041] **FIG. 9** is an enlarged cross-sectional view showing the fixing portion of a vibration vane to the vibration transmitting rod of the continuously electrolyzing apparatus of **FIG. 1**;

[0042] **FIG. 10** is a plan view showing a modification of the vibration vane and the fixing member;

[0043] **FIG. 11** is a plan view showing a modification of the vibration vane and the fixing member;

[0044] **FIG. 12** is a plan view showing a modification of the vibration vane and the fixing member;

[0045] **FIG. 13** is a plan view showing a modification of the vibration vane and the fixing member;

[0046] **FIG. 14** is a graph showing the relationship between the length and flexibility of the vibration vane;

[0047] **FIG. 15** is a cross-sectional view showing a modification of the vibrating flow generator;

[0048] **FIG. 16** is a cross-sectional view showing a modification of the vibrating flow generator;

[0049] **FIG. 17** is a cross-sectional view showing a modification of the vibrating flow generator;

[0050] **FIG. 18** is a cross-sectional view showing a modification of the vibrating flow generator;

[0051] **FIG. 19** is a cross-sectional view showing a modification of the vibrating flow generator;

[0052] **FIG. 20** is a cross-sectional view showing a fixing manner of the vibrating flow generator to the electrolytic tank in a continuously electrolyzing apparatus in which the waste liquid continuously electrolyzing method of the present invention is carried out;

[0053] **FIG. 21** is a cross-sectional view showing the continuously electrolyzing apparatus of **FIG. 20**;

[0054] **FIG. 22** is a plan view showing the continuously electrolyzing apparatus of **FIG. 20**;

[0055] **FIGS. 23A** to **23**C are plan views of a laminate member;

[0056] **FIGS. 24A and 24B** are cross-sectional views showing the sealing state of the electrolytic tank by the laminate member;

[0057] **FIGS. 25A** to **25**E are cross-sectional views showing various embodiments of the laminate member;

[0058] **FIG. 26** is a partially-omitted plan view showing the construction of a continuously electrolyzing apparatus in which the waste liquid continuously electrolyzing method of the present invention is carried out;

[0059] **FIG. 27** is a cross-sectional view showing the continuously electrolyzing apparatus of **FIG. 26**; and

[0060] **FIG. 28** is a cross-sectional view showing the continuously electrolyzing apparatus of **FIG. 26**.

PREFERRED EMBODIMENTS FOR IMPLEMENTING THE INVENTION

[0061] Embodiments of the present invention will be described with reference to the accompanying drawings. In the drawings, the members and parts having the same functions are represented by the same reference numerals.

[0062] FIGS. **1** to **5** show the construction of an embodiment of a continuously electrolyzing apparatus in which a method for continuously electrolyzing waste liquid of the present invention is carried out. Here, **FIG. 1** is a plan view, **FIGS. 2 and 3** are cross-sectional views, **FIG. 4** is a partially-omitted plan view and **FIG. 5** is a partially-omitted cross-sectional view.

[0063] In these figures, two electrolytic cells or electrolytic tanks **10**A and **10**B are unified to constitute an array or series **10** of electrolytic tanks. The series **10** forms a tank as a whole, and the electrolytic tank **10**A and the electrolytic tank **10**B are partitioned by a partition wall **11**. Waste liquid **14** to be treated is supplied into the electrolytic tanks **10**A and **10**B.

[0064] In the series **10**, the electrolytic tanks **10**A and **101**B are connected to each other in series (the in-series connection means the link style with respect to the flow of waste liquid, and indicates that the waste liquid flows through plural electrolytic tanks in turn). That is, a waste liquid supply pipe **12**A for supplying waste liquid to be treated from the external is connected to one electrolytic tank **10**A, and a waste liquid take-out pipe **12**B for taking out treated waste liquid to the external is connected to the other electrolytic tank **10**B. Further, a chute **13** for feeding the waste liquid **14** in the electrolytic tank **10**A to the electrolytic tank **10**B is equipped along the upper end edge of the partition wall **11** between the electrolytic tanks **10**A and **11**B. In the chute **13**, a flow-in cut-out portion **13***a* for allowing the waste liquid **14** to flow in from the electrolytic tank **10**A is armed in the wall thereof at the electrolytic tank (**10**A) side at one end thereof in the longitudinal direction, and a flow-out cut-out portion **13***b* for allowing the waste liquid **14** to flow out to the electrolytic tank **10**B is formed in the wall thereof at the electrolytic tank (**10**B) side at the other end thereof in the longitudinal direction.

[0065] Further, a dam **15** is disposed adjacently to the flow-in cut-out portion **13***a* in the electrolytic tank **10**A. The dam **15** serves to prevent the waste liquid **14** in the electrolytic tank **10**A from flowing into the chute **13** excessively or timely unevenly, and it is fixed to the wall and bottom of the electrolytic tank **10**A.

[0066] **FIG. 6** is a partially-omitted perspective view showing the neighborhood of the flow-in cut-out portion **13***a*. In order to assist the flow of the waste liquid **14** from the flow -in cut-out portion **13***a* to the flow-out cut-out portion **13***b* through the chute **13**, the chute **13** is preferably designed to be gradually inclined downwardly from the flow- in cut-out portion (**13***a*) side to the flow-out cut-out portion (**13***b*) side. In **FIGS. 4 and 6**, the flow direction of the waste liquid **14** is indicated by arrows.

[0067] Various kinds of FRP, passive stainless steel chemical-resisting iron, enamel or the like may be used as the material of the electrolytic tanks **10**A, **10**B, the chute **13** and the dam **15**.

[0068] Reference numeral **16** represents a vibrating flow generator as vibrating flow generating means. The vibrating flow generator **16** has a base table **16***a* fixed to the electrolytic tanks **10**A, **10**B through a rubber vibration insulator, coil springs **16***b* as a vibration absorber fixed to the base table at the lower ends thereof, a vibrating member **16***c* fixed to the upper end of the coil spring, a vibration motor **16***d* as vibration generating means fixed to the vibrating member, vibration transmitting rods **16***e* fixed to the vibrating member **16***c* at the upper ends thereof and vibrating vanes **16***f* fixed to the lower half portions of the vibration transmitting rods so as to be immersed in the waste liquid **14**. Rod-shaped upper and lower guide members may be disposed in each of the coil springs **16***b* to prevent side slipping of the springs as shown in **FIGS. 16 and 17**. In place of the coil springs **16***c*, a buffer such as rubber or the like may be used.

[0069] The vibration motor **16***d* is vibrated at a frequency of 10 to 500 Hz, particularly at a frequency of 10 to 150 Hz, preferably at a frequency of 20 to 100 Hz and more preferably at a frequency of 40 to 60 Hz under the control based on an inverter or the like. The vibration generated by the vibration motor **16***d* is transmitted to the vibrating vanes **16***f* through the vibrating member **16***c* and the vibration transmitting rods **16***e*. The vibrating vanes **16***f* are vibrated at the tip edges thereof at a required frequency in the waste liquid **14**. This vibration is generated so that the vibrating vanes **16***f* flutters from the fixing portions thereof to the vibration transmitting rods **16***e* to the tip edges thereof. The amplitude and frequency of the vibration of the vibrating vanes are different from those of the vibration motor **16***d*, and they are determined by the dynamic characteristic of vibration transmitting route and the interacting characteristic with the waste liquid **14**. In the present invention, it is preferable that the amplitude is set to 0.05 to 10.0 mm (for example, 0.1 to 10.0 mm, particularly 2 to 8 mm) and the vibration frequency is set to 100 to 1500 cycles per minute (for example, 100 to 1000 cycles per minute).

[0070] **FIG. 7** is an enlarged cross-sectional view showing the fixing portion **111** of the vibration transmitting rod **16***e* to the vibrating member **16***c*.

[0071] As shown in **FIG. 7**, nuts **16***i***1**, **16***i***2** are fitted to a male screw portion formed on the upper end of each vibration transmitting rod **16***e* through a vibrating stress dispersing member **16***g***1** and a washer **16***h* from the upper side of the vibrating member **16***c*, and nuts **16***i***3**, **16***i***4** are fitted to the male screw portion through a vibrating stress dispersing member **16***g***2** from the lower side of the vibrating member **16***c*.

[0072] The vibrating stress dispersing members **16***g***1**, **16***g***2** are used as the vibrating stress dispersing means, and it is formed of rubber, for example. The vibrating stress dispersing members **16***g***1**, **16***g***2** may be formed of a hard elastic member of 80 to 120, preferably 90 to 100 in Shore A hardness, such as hard natural rubber, hard synthetic rubber, synthetic resin or the like. Particularly, hard urethane rubber of 90 to 100 in Shore A hardness is preferably used from the viewpoint of durability and chemical resistance. By using the vibrating stress dispersing means, the vibrating stress can be prevented from concentrating on the neighborhood of the joint portion between the vibrating member **16***c* and the vibration transmitting rod **16***e*, and the vibration transmitting rod **16***e* is hardly broken. Particularly, when the vibration frequency of the vibration motor **16***d* is set to 100 Hz or more, the breakage preventing effect of the vibrating transmitting rod **16***e* is remarkable.

[0073] **FIG. 8** is an enlarged cross-sectional view showing a modification of the fixing portion **111** of the vibration transmitting rod **16***e* to the vibrating member **16***c*. This modification is different from the fixing portion of **FIG. 7** only in that the vibrating stress dispersing member **16***g***1** is not disposed at the upper side of the vibrating member **16***c* and a spherical spacer **16***x* is interposed between the vibrating member **16***c* and the vibrating stress dispersing member **16***g***2**, and the other parts are the same.

[0074] **FIG. 9** is an enlarged cross-sectional view showing the fixing portion of each vibrating vane **16***f* to the vibration transmitting rod **16***e*. Vibrating vane fixing members **16***j* are disposed at both the upper and lower sides of each vibrating vanes **16***f*. Spacer rings **16***k* for setting the interval between the neighboring vibrating vanes **16***f* are disposed through the fixing members **16***j* between the neighboring vibrating vanes **16***f*. As shown in **FIGS. 2 and 3**, nuts **16***m* fitted to the male screws formed on each vibrating transmitting rods **16***e* are disposed at the upper side of the uppermost vibrating vane

16*f* and at the lower side of the lowermost vibrating vane **16***f* through the spacer rings **16***k* or through no spacer ring.

[**0075**] As shown in **FIG. 9**, an-elastic member sheet **16***p* serving as the vibrating stress dispersing means formed of fluorine-based resin, fluorine-based rubber or the like is interposed between each vibrating vane **16***f* and each fixing member **16***j* to prevent breakage of the vibrating vane **16***f*. In order to further enhance the breakage preventing effect of the vibrating vane **16***f*, the elastic member sheet **16***p* is preferably disposed so as to slightly protrude from the fixing member **16***j*. As shown in **FIG. 9**, the lower surface (pressing face) of the upper fixing member **16***j* is designed in a convex shape and the upper surface (pressing face) of the lower fixing member **16***j* is designed in the corresponding concave shape. Accordingly, the portion of the vibrating vane **16***f* which are pressed from the upper and lower sides by the firing members **16***j* is bent, and the tip portion of the vibrating vane **16***f* intersects to the horizontal plane at an angle of α. The angle α may be set to a value in the range from −30° to 30°, and preferably in the range from −20° to 20°. Particularly, the angle α is set to a value in the range from −30° to −5° or 5° to 30°, preferably in the range from −20° to −10° or 10° to 20°.

[**0076**] When the pressing face of the fixing member **16***j* is designed to be flat, the angle α is equal to 0°. It is unnecessary for all the vibrating vanes **16***f* to have the same angle α, and for example, the angle α of several lower vibrating vanes **16***f* is set to a minus value (that is, face down: oriented in the direction as shown in **FIG. 9**), and the angle α of the other vibrating vanes **16***f* is set to a plus value (that is, face up: oriented in the opposite direction to the direction shown in **FIG. 9**).

[**0077**] FIGS. **10** to **13** are plan views showing modifications of the vibrating vane **16***f* and, the fixing member **16***j*. In the modifications shown in **FIGS. 10 and 11**, the vibrating vane **16***f* may be constructed by two strip members stacked orthogonally to each other, or may be constructed by cutting out one plate in a cross shape.

[**0078**] A metal plate, a synthetic resin plate or a rubber plate which are elastic may be used as the vibrating vane **16***f*. The preferable thickness range of the vibrating vane **16***f* is varied in accordance with the vibration condition, the viscosity of the waste liquid **14**, etc., and it is set so that the tip portion of each vibrating vane **16***f* shows a "flutter phenomenon" (undulating state) with no breakage of the vibrating vane and the vibrating flow stirring efficiency is enhanced when the vibrating flow generator **16** is actuated. When the vibrating vane **16***f* is formed of metal plate such as stainless steel plate or the like, the thickness thereof may be set to 0.2 to 2 mm. Further, when the vibrating vane **16***f* is formed of synthetic resin plate or rubber plate, the thickness thereof may be set to 0.5 to 10 mm. A member achieved by integrally molding the vibrating vane **16***f* and the fixing member **16***j* may be used. In this case, there can be avoided such a problem that the waste liquid **14** infiltrates into the joint portion between the vibrating vane **16***f* and the fixing member **16***j* and solid materials are firmly fixed so that cleaning takes a lot of trouble.

[**0079**] As the material of the metal vibrating vane **16***f* may be used titanium, aluminum, copper, steel, stainless steel magnetic metal such as magnetic steel or the like, and alloys of these materials. As the material of the synthetic resin vibrating vane **16***f* may be used polycarbonate, vinyl-chloride resin, polypropylene, etc.

[**0080**] The degree of the "flutter phenomenon" of the vibrating vane which occurs due to the vibration of the vibrating vane **16***f* in the waste liquid **14** is varied in accordance with the vibration frequency of the vibration motor **16***d*, the length (the dimension from the tip edge of the fixing member **16***j* to the tip edge of the vibrating vane **16***f*) and thickness of the vibrating vane **16***f*, the viscosity and specific gravity of the waste liquid **14**, etc. The length and thickness of the vibrating vane **16***f* at which the vibrating vane flutters most at a given frequency can be selected. If the vibration frequency of the vibration motor **16***d* and the thickness of the vibrating vane **16***f* are fixed and the length of the vibrating vane **16***f* is varied, the fluttering degree is shown in **FIG. 14**. That is, as the length m is increased, the fluttering degree F. is increased up to some stage. However, when the length m exceeds this stage, the fluttering degree F. is reduced the vibrating vane is little fluttered when the length m is equal to some value. Further, when the length of the vibrating vane is further increased, the fluttering degree F. is increased again. This phenomenon is repeated.

[**0081**] With respect to the length of the vibrating vane, the length L_1 showing the first peak or the length L_2 showing the second peak is preferably selected. Which one of the length L_1 and the length L_2 should be selected can be determined at pleasure in accordance with which one of the vibration and flow of the system should be intensified. When the length L_3 showing the third peak is selected, the amplitude is liable to be reduced. L_1 and L_2 were measured for vibrating vane of stainless steel (SUS304) by using a 75 kW vibration motor having a vibration frequency 40 to 60 Hz (manufactured by Murakami Seiki MFG. Co., Ltd.) while varying the thickness of the vibrating vane, and the measurement results are shown in the following Table 3.

TABLE 3

THICKNESS	L_1	L_2
0.10 mm	about 15 mm	—
0.20 mm	about 25 mm	about 70 mm
0.30 mm	about 45 mm	110–120 mm
0.40 mm	about 50 mm	110–120 mm
0.50 mm	about 55 mm	

[**0082**] In this experiment, the length from the center of the vibration transmitting rod **16***e* to the tip edge of the fixing member **16***j* was set to 27 mm, and the inclination angle α of the vibrating vane **16***f* was set to face-up 15° (+15°).

[**0083**] Returning to **FIG. 3** again, according to this embodiment, the vibration generated by one vibration motor **16***d* is transmitted to the vibrating vanes **16***f* disposed in the electrolytic tanks **10**A, **10**B, that is, one vibration motor **16***d* is commonly used for the vibrating flow generating means of the electrolytic tanks **10**A, **10**B.

[**0084**] Next, as shown in **FIGS. 1 and 2**, plural anode bus bars **20** and plural cathode bus bars **21** are disposed on the electrolytic tanks **10**A, **10**B. These bus bars are connected to the positive and negative terminals of a power supply circuit **34** serving as an electrolysis power source, respectively. Plural plate-shaped anodes **22** are suspended on each anode bus bar **20**, and the lower portions of the anodes **22** are immersed in the waste liquid **14**. Likewise, plural plate-shaped cathodes **23** are suspended on each cathode bus bar **21**, and the lower portions of the cathodes **23** are immersed in the waste liquid **14**. The anodes **22** and the cathodes **23** are alternately arranged at predetermined intervals. The distance between the electrodes (anode and cathode) is preferably set to 5 to 50 mm, more preferably 10 to 40 mm, and particularly more preferably 20 to 30 mm.

[**0085**] In the present invention, the vibrating flow stirring of the waste liquid **14** is carried put by the vibrating flow generating means, thereby suppressing explosion caused by the reaction of hydrogen and oxygen generated at the electrodes, so that the distance between the electrodes can be reduced to such a small value.

[**0086**] The ratio (electrode ratio) in area between the immersed portion of the cathode **23** in the waste liquid **14** and the immersed portion of the anode **22** in the waste liquid **14** is set so that the cathode is equal to 0.5 or more with respect to the anode of 1, more preferably the cathode is equal to 0.6 to 0.9 with respect to the anode of 1. In the present invention, it is preferable that a part of each anode **22** (particularly, the portion immersed in the waste liquid **14**) is designed in a mesh or porous structure to enhance the fluidity of the waste liquid **14**. Further, the area of the mesh or porous portion is preferably set to 10 to 80% with respect to the area of the portion immersed in the waste liquid **14**, and more preferably 50 to 80%.

[**0087**] In the present invention, the voltage applied between the anode **22** and the cathode **23** by the power supply circuit **34** is preferably set to 4 to 15V, more preferably to 5 to 6 V. Further, the current flowing between the anode **22** and the cathode **23** is set to 0.8 to 5A per liter of the waste liquid **14**, and more preferably to 1.5 to 2A, for example, and the optimum value is varied in accordance with the kind of the waste liquid **14**.

[**0088**] In the above-described embodiment, the waste liquid **14** to be treated is continuously supplied to the electrolytic tank **10**A through the waste liquid supply pipe **12**A. The waste liquid **14** to be treated overflowing from the electrolytic tank **10**A flows from the flowing cut-out portion **13***a* into the chute **13**, and then flows from the flow-out cut-out portion **13***b* into the electrolytic tank **10**B. The waste liquid **14** to be treated which overflows from the electrolytic tank **10**B is taken out as treated waste liquid through the waste liquid take-out pipe **12**B.

[**0089**] As described above, the vibration motor **16***d* of the vibrating flow generator **16** is made to vibrate while the waste liquid **14** is continuously supplied into the series **10** of the tanks, whereby the vibrating vanes **16***f* fixed to the vibration transmitting rods **16***e* operationally connected to the vibration motor **16***d* so as to vibrate in the waste liquid **14** is vibrated in each of the electrolytic tanks **10**A, **10**B, thereby producing the vibrating flow in the waste liquid **14**. Further, a predetermined voltage is applied between the anode **22** and the cathode **23** through the anode bus bar **20** and the cathode bus bar **21** by the power supply circuit **34** to electrolyze the waste liquid **14** in the electrolytic tanks **10**A, **10**B.

[**0090**] As the waste liquid to be treated by the continuous treatment method and apparatus of the present invention may be cited metal-contained waste liquid such as waste liquid containing transition metal and/or alloy thereof, for example, waste liquid containing at least one of elements having atomic numbers of 21 (Sc) to 30 (Zn), 39 (Y) to 48 (Cd) and 57 (La) to 80 (Hg). As typical waste liquid may be cited waste liquid containing Ti, V, Cr, Mn, Fe, Co and/or Ni. Further, cyanogen-contained waste liquid may be cited as the waste liquid to be treated. Cyanogen-contained waste liquid can be decomposed into carbon dioxide, nitrogen and water by electrolytic oxidation.

[**0091**] In the present invention, even when the distance between the anode **22** and the cathode **23** is reduced and the current density is increased, occurrence of short-circuiting is suppressed and further occurrence of explosion caused by the reaction of hydrogen and oxygen generated from the electrodes is suppressed by the action of the vibrating flow generated in the waste liquid **14**. Therefore, the continuous electrolyzing treatment can be efficiently and quickly performed on the waste liquid **14** with sufficiently high current density. In order to achieve such an action excellently, it is preferable to produce the vibrating flow so that the three-dimensional flow velocity of the waste liquid **14** is equal to 150 mm/second or more. The three-dimensional flow velocity of the waste liquid **14** is preferably equal to 200 mm/second or more, and more preferably to 250 mm/second or more. The three-dimensional flow velocity can be measured by using a three-dimensional electromagnetic flow velocity detector (trade name: ACM300 manufactured by Alec Electronics Co., Ltd.). Such a high three-dimensional flow velocity can be effectively achieved by inducing the vibrating flown the waste liquid **14**. It is difficult to implement such vibrating flow by normal stirring, and a large-scale apparatus architecture is required in order to implement the vibrating flow.

[**0092**] **FIG. 15** is a cross-sectional view showing a modification of the vibrating flow generator. In this modification, the base table **16***a* is fixed onto a fixing table **40** fixed to the upper portion of the electrolytic tank **10**A through a vibration absorbing member **41**. Further, rod-like guide members **43** extending upwardly in the vertical direction are fixed to the fixing table **40**, and the guide members **43** are located in the coil springs **16***b*. A transistor inverter **35** for controlling the vibration frequency of the vibration motor **16***d* is interposed between the vibration motor **16***d* and a power source **136** for driving the vibration motor. The voltage supplied from the power source **136** is equal to 200V for example. Such driving means of the vibration motor **16***d* can be used in the other embodiments of the present invention.

[**0093**] **FIG. 16** is a cross-sectional view showing a modification of the vibrating flow generator. In this modification, rod-like upper guide members **144** extending downwardly in the vertical direction are fixed to the vibrating member **16***c*, rod-like lower guide members **145** extending upwardly in the vertical diction are fixed to the fixing table **40**, and these guide members **144**, **145** are located in the coil springs **16***b*. Further, a proper gap for allowing vibration of the vibrating member **16***c* is formed between the lower end of the upper guide member **144** and the upper end of the lower guide member **145**.

[**0094**] **FIG. 17** is a cross-sectional view showing a modification of the vibrating flow generator. In this modification, the vibration motor **16***d* is fixed to the lower side of an additive vibrating member **16***c*' equipped to the upper side of the vibrating member **16**. The vibration transmitting rod **16***e* is branched into two portions **134** in the electrolytic tank **10**A, and the vibrating vanes **16***f* are fixedly bridged between the two rod portions **134**.

[0095] **FIGS. 18 and 19** are cross-sectional views showing a modification of the vibrating flow generator. In this modification, the lowermost vibrating vane **16***f* is inclined downwardly, and the other vibrating vanes **16***f* are inclined upwardly. This construction enables sufficient vibrating flow stirring of the waste liquid **14** at a portion near to the bottom portion of the electrolytic tank **10**A, and occurrence of pooling at the bottom portion of the electrolytic tank can be prevented. Further, by inclining all the vibrating vanes **16***f* downwardly, hydrogen and oxygen generated through the electrolysis can be sufficiently scattered into the waste liquid to thereby increase the frequency of the reaction opportunity with metals and cyanogen.

[0096] **FIGS. 20 and 21** are cross-sectional views showing another fixing manner of the vibrating flow generator to the electrolytic tank in the continuous electrolyzing apparatus in which the method for continuously electrolyzing waste liquid of the present invention is carried out, and **FIG. 22** is a plan view of the continuous electrolyzing apparatus. **FIGS. 20 and 21** correspond to the X-X' cross-sectional view and the Y-Y' cross-sectional view of **FIG. 22**, respectively. In these figures, the cathode, the anode, the power supply circuit, etc. for the electrolysis are omitted from illustration.

[0097] In this embodiment, in place of the coil springs **16***b*, a laminate member **3** comprising a rubber plate **2** and metal plates **1, 1'** is used as the vibration absorbing member. That is, the laminate member **3** is formed as follows. That is, the metal plate **1'** is fixed-through a rubber vibration insulator **112** by bolts **131** to a fixing member **118** fixed to the upper end edge portion of the electrolytic tank **10**A, the rubber plate **2** is disposed on the metal plate **1'**, the metal plate **1** is disposed on the rubber plate **2** and these parts are unified into one body by bolts **116** and nuts **117**.

[0098] The vibration motor **16***d* is fixed to the metal plate **1** through a support member **115** by bolts **132**. The upper end portion of the vibration transmitting rod **16***e* is fixed through a rubber ring **119** to the laminate member **3**, particularly to the metal plate **1** and the rubber plate **2**. That is, the upper metal plate **1** also exhibits the function of the vibrating member **16***c* of the embodiments described with reference to **FIG. 1** and the other figures, and the lower metal plate **1'** exhibits the function of the base table **16***a* of the embodiments described with reference to **FIG. 1** and the other figures. The laminate member **3** (mainly the rubber plate **2**) containing the metal plates **1, 1'** exhibits the same vibration absorbing function as the coil springs **16***b* described with reference to **FIG. 1** and the other figures.

[0099] **FIGS. 23A** to **23**C are plan, views showing the laminate member **3**.

[0100] In an embodiment of **FIG. 23A** corresponding to the embodiment shown in FIGS. **20** to **22**, through holes **5** through which the vibration transmitting rods **16***e* penetrate are formed in the laminate member **3**. In an embodiment of **FIG. 23**B, the laminate member **3** comprises two portions **3***a* and **3***b* into which the laminate member **3** is divided by a dividing the passing through the through holes **5**. With this construction, the vibration transmitting rods **16***e* can be made to easily penetrate through the through holes when the apparatus is fabricated. In an embodiment of **FIG. 23**C, the laminate member **3** has an annular shape corresponding to the upper end edge portion of the electrolytic tank **10**A, and an opening **6** is formed at the center of the laminate member **3**.

[0101] In the embodiments of **FIGS. 23A and 23B**, the upper portion of the electrolytic tank **10**A is sealed by the laminate member **3**, whereby gas volatilized from the waste liquid **14** or splashing electrolytic solution can be prevented from leaking to the surrounding.

[0102] **FIGS. 24A and 24B** are cross-sectional views showing the sealing state of the electrolytic tank by the laminate member **3**. In the embodiment of **FIG. 24**A, the rubber plate **2** abuts against the vibration transmitting rod **16***e* in the through hole **5** to perform sealing. In the embodiment of **FIG. 24B, a** flexible seal member **136** which is fixed to the laminate member **3** and the vibration transmitting rod **16***e* and doses the gap between these elements is equipped to the opening portion **6** of the laminate member **3**.

[0103] **FIGS. 25A** to **25**E each show an embodiment of the laminate member **3** as a vibration absorbing member.

[0104] The embodiment of **FIG. 25B** corresponds to the embodiment of FIGS. **20** to **22**. In the embodiment of **FIG. 25**A, the laminate member **3** comprises a metal plate **1** and a rubber plate **2**. In the embodiment of **FIG. 25**C, the laminate member **3** comprises an upper metal plate **1**, an upper rubber plate **2**, a lower metal plate **1'** and a lower rubber plate **2'**. In the embodiment of **FIG. 25**D, the laminate member **3** comprises an upper metal plate **1**, an upper rubber plate **2**, an intermediate metal plate **1"**, a lower rubber plate **2'** and a lower metal plate **1'**. The number of metal plates and the number of rubber plates in the laminate member **3** may be set to 1 to 5, for example. In the present invention, the vibration absorbing member may be constructed by only rubber plate.

[0105] Stainless steel iron, copper, aluminum or other proper alloy may be used as the material of the metal plates **1, 1', 1"**. The thickness of the metal plate may be set to 10 to 40 mm, for example. However, the metal plate (for example, the intermediate metal plate **1"**) which is not directly fixed to the members other than the laminate member **3** may be set to a small value for example, 0.3 to 10 mm).

[0106] Synthetic rubber or vulcanized natural rubber may be used as the material of the rubber plates **2, 2'**. Rubber vibration insulator defined by JISK6386 is preferably used, and more preferably the rubber plates are formed of materials of 4 to 22 kgf/cm^2, preferably 5 to 10 kgf/cm^2 in static modulus of elasticity in shear and 250% or more in ultimate elongation. As the synthetic rubber may be used chloroprene rubber, nitrile rubber nitrile-chloroprene rubber, styrene-chloroprene rubber, acrylonitrile-butadiene rubber, isoprene rubber, ethylene-propylene-diene copolymer rubber, epichlorohydrin rubber, alkylene oxide rubber, fluorine rubber, silicone rubber, urethane rubber, polysulfide rubber, phosphorus rubber (flame-retarded rubber) or the like. The thickness of the rubber plate is set to 5 to 60 mm, for example.

[0107] In the embodiment of **FIG. 25**E, the laminate member **3** comprises an upper metal plate **1**, a rubber plate

2 and a lower metal plate **1'**, and the rubber plate **2** comprises an upper solid rubber layer **2***a*, a sponge rubber layer **2***b* and a lower solid rubber layer **2***c*. One of the upper and lower solid rubber layers **2***a*, **2***c* may be removed. Further, plural solid rubber layers and plural sponge rubber layers may be laminated.

[**0108**] FIGS. **26** to **28** show the construction of another embodiment of the continuously electrolyzing apparatus in which the method for continuously electrolyzing waste liquid according to the present invention is executed. Here, **FIG. 26** is a partially-omitted plan view, and **FIGS. 27 and 28** are cross-sectional views.

[**0109**] In this embodiment, the series **10** of tanks contains three electrolytic tanks **10**A, **10**B, **10**C connected to one another in series, and a partition wall **11** and a chute **13** are disposed between the electrolytic tanks **10**A, **10**B and between the electrolytic tanks **10**B and **10**C, respectively. The vibration motor **16***d* is commonly used for the vibrating flow generating means of the three electrolytic tanks **10**A, **10**B, **10**C. In each of the electrolytic tanks **10**A, **10**B, **10**C, the same electrolysis as the above embodiments is carried out, and the waste liquid **14** supplied to the electrolytic tank **10**A through the waste liquid supply pipe **12**A is taken out from the electrolytic tank **10**C through the waste liquid take-out pipe **12**B.

[**0110**] In this embodiment, the continuous electrolysis using the three electrolytic tanks **10**A, **10**B, **10**C is carried out, and thus waste liquid of higher concentration can be sufficiently electrolyzed. Further, the number of electrolytic tanks can be increased as occasion demands.

[**0111**] Next, the present invention will be described with the following Examples, however, the present invention is not limited to these Examples.

EXAMPLE 1

[**0112**] The continuous electrolysis of chromium plating waste liquid was carried out by using the three-tank type apparatus for continuously electrolyzing waste liquid shown in FIGS. **26** to **28**. The construction of the apparatus and the operating condition were as follows.

[**0113**] Vibration motor: 3-phase, 200V 250W (URAS VIBRATOR 2-pole KZE type manufactured by Murakami Seiki MFG. Co., Ltd.)

[**0114**] Inverter: Fuji inverter FVR-CIIS manufactured by Fuji Electric Co., Ltd.

[**0115**] Power source for vibration motor: (H-mini MB-7 silicon rectifier) 6.0 kW manufactured by Chuo Seisakusho Co., Ltd.

[**0116**] Capacity of electrolytic tank (total of three tanks): 520 liters

[**0117**] Vibrationally stirring condition: vibration frequency of vibration motor was regulated to 45 Hz by the inverter; amplitude of 0.15 mm, frequency of 200 cycles per minute of the vibrating vanes

[**0118**] Anode: iron plate

[**0119**] Cathode: platinum plate

[**0120**] Anode/cathode distance: 30 mm

[**0121**] Electrode ratio: cathode/anode=1/1.5≈0.67

[**0122**] Voltage for electrolysis 4V

[**0123**] Current for electrolysis: 450A (=0.865A/waste liquid of 1 liter)

[**0124**] The waste liquid to be treated was chromium plating waste liquid (containing trivalent chromium of about 1000 ppm) whose pH was adjusted to 2.5 by sulfuric acid, and it was supplied into a series of the three electrolytic tanks at a rate of 1000 liters/hour to carry out the continuous electrolysis.

[**0125**] The concentration of trivalent chromium in the treated waste liquid picked up from the waste liquid take-out port was equal to 0 ppm. It is estimated that by carrying out the vibrating flow stirring, sufficiently activated hydrogen gas generated from the electrode attacks hexavalent chromium existing in the waste liquid to reduce hexavalent chromium to trivalent chromium in extremely short time, and the trivalent chromium thus reduced is reacted with sulfuric acid in the waste liquid to form chromium sulfate $CrSo_4$.

EXAMPLE 2

[**0126**] The continuous electrolysis of waste liquid containing cyanogen was carried out by using the two-tank type apparatus for continuously electrolyzing waste liquid shown in FIGS. **1** to **5**. The construction of the apparatus and the operating condition were the same as Example 1 with the exception of the following points.

[**0127**] Capacity of electrolytic tank (total of two tanks): 330 liters

[**0128**] Anode: titanium plate whose surface was deactivated by PbO_2 (carbon or graphite maybe used)

[**0129**] Cathode: stainless steel plate (SUS340) (Pt or In may be used)

[**0130**] Cathode/cathode distance: 25 mm

[**0131**] Electrode ratio: cathode/anode=0.8/1=0.8

[**0132**] Current for electrolysis: 450A (=1.364A waste liquid of 1 liter)

[**0133**] The waste liquid to be treated was cyanogen-contained waste liquid of 2000 ppm in cyanogen concentration whose pH was adjusted to 10 by caustic soda, and it was supplied into a series of the two electrolytic tanks at a rate of 500 liters/hour to carry out the continuous electrolysis.

[**0134**] The concentration of cyanogen in the treated waste liquid picked up from the waste liquid take-out port was equal to 1 ppm. Cyanogen was decomposed into carbon dioxide and N_2 in the treatment.

EXAMPLE 3

[**0135**] Waste liquid generated from the plating treatment of a plastic substrate was continuously electrolyzed by using the two tank type apparatus for continuously waste liquid shown in FIGS. **1** to **5**. The construction of the apparatus and the operating condition were the same as Example 2 with the exception of the following points.

[0136] Anode: stainless steel plate (SUS340) (platinum may be used)

[0137] Cathode: copper plate (copper-plated plate may be used)

[0138] Anode/cathode distance 30 mm

[0139] Electrode ratio: cathode/anode=0.5/1=0.5

[0140] Voltage for electrolysis: 12V

[0141] Current for electrolysis: 300A (=0.909A/waste liquid of 1 liter)

[0142] Waste liquid to be treated was obtained as follows.

[0143] Plating treatment was carried out on a plastic substrate by using copper sulfate plating bath comprising the following materials:

copper sulfate ($CuSO_4 \cdot 5H_2O$)	60 g/liter
sulfuric acid (H_2SO_4)	200 g/liter
chlorine ion (Cl^-)	60 mg/liter

[0144] and then the result generated from the above plating treatment was adjusted by sulfuric acid to set to the pH value to 2 and the concentration of copper sulfate to 150 mg/liter, and the result was added with NaCl (KCl may be used) as electrolysis auxiliary agent at a ratio of 200 g/liter. The result thus achieved was supplied as waste liquid into a series of the two electrolytic tanks at a rate of 500 liter/hour to perform the continuous electrolysis.

[0145] The concentration of copper in the treated waste liquid taken out from the waste liquid take-out port was equal to 1 ppm.

EXAMPLE 4

[0146] The continuous electrolysis was carried out on Zn plating bath by using the two-tank type apparatus for continuously electrolyzing waste liquid shown in FIGS. **1** to **5**. The construction of the apparatus and the operating condition were the same as Example 3 with the exception of the following points.

[0147] Cathode: Zn thin plate (Zn steel plate may be used)

[0148] The waste liquid to be treated was Zn plating bath (zincate bath) containing Zn of 500 ppm, and it was supplied into a series of the two electrolytic tanks at a rate of 500 liter/hour to perform the continuous electrolysis treatment.

[0149] The Zn concentration in the treated waste liquid collected from the waste liquid take-out port was equal to 3 ppm.

[0150] The same effect was achieved when the continuous electrolysis was carried out on waste liquid containing transition metals such as Ni, Ag, Au, Sn, Fe, etc. and/or alloys thereof in the same manner as the above Examples.

[0151] Particularly, the present invention is effective on the treatment of waste liquid containing ferrous chloride generated as a result of photomicrofabrication, and ferrous chloride in waste liquid can be continuously electrolytically reduced and withdrawn as ferric chloride. Therefore, the ferric chloride thus withdrawn can be applied to photomicrofabrication again.

INDUSTRIAL APPLICABILITY

[0152] (1) The present invention can be applied irrespective of the concentration of metals in waste liquid, no sludge occurs and the metals can be withdrawn and recycled.

[0153] (2) The present invention can greatly reduce the running cost to 1/20 to 1/100 with respect to the conventional treatment using chemicals because no chemical is used and efficiency of the treatment is high.

[0154] (3) In the present invention, the treatment time from the supply to the take-out of the waste liquid into/out of a series of the tanks is equal to about 20 to 40 minutes, and this time is short. In addition, although it has been hitherto estimated that it is impossible to perform the waste liquid electrolysis by using any treatment method other than the batch treatment, however, it is the first time that the present invention succeeds to continuously perform the waste liquid electrolysis.

[0155] (4) In the present invention, when cyanogen-contained waste liquid is treated, cyanogen is decomposed into carbon dioxide gas and N_2, and no ammonia occurs.

[0156] (5) The apparatus is very simple in construction, and no specific electrode plate is needed.

[0157] (6) In the case of a treatment using chemicals, a secondary trouble such as failure of aggregation or the like occurs. However, no such trouble occurs in the present invention.

[0158] (7) In the case of chromium-contained waste liquid, the conventional treatment method using chemicals produces foul odors because it uses sodium bisulfite, however no foul odor occurs in the present invention.

What is claimed is:

1. A method for continuously electrolyzing waste liquid, comprising the steps of:

continuously supplying waste liquid to be treated into a first electrolytic tank of a series of tanks comprising a plurality number n (n represents an integer equal to or greater than 2) of electrolytic tanks each having an anode and a cathode, the electrolytic tanks being connected in series; and

continuously talking out treated waste liquid from an n-th electrolytic tank of the series of tanks,

wherein a voltage is applied between the anode and the cathode in each tank to electrolyze the waste liquid to be treated under the state that vibrating vanes fixed to vibrating rods which are operationally connected to vibration generating means so as to vibrate in the waste liquid to be treated are vibrated at an amplitude of 0.05 to 10.0 mm and at an oscillation frequency of 100 to 1500 cycles per minute to induce vibrating flow in the waste liquid to be treated.

2. The method for continuously electrolyzing waste liquid as claimed in claim 1, wherein the vibrating flow is generated so that the three-dimensional flow velocity of the waste liquid to be treated is equal to 150 mm/second or more.

3. The method for continuously electrolyzing waste liquid as claimed in claim 1, wherein the vibration generating means is vibrated at a frequency of 10 to 500 Hz.

4. The method for continuously electrolyzing waste liquid as claimed in claim 1, wherein the distance between the anode and the cathode is kept to be equal to 5 to 50 mm.

5. The method for continuously electrolyzing waste liquid as claimed in claim 1, wherein a voltage of 4 to 15V is applied between the anode and the cathode.

6. An apparatus for continuously electrolyzing waste liquid, comprising:

a series of tanks comprising a plurality number n (n represents an integer equal to or greater than 2) of electrolytic tanks each having an anode and a cathode, the electrolytic tanks being connected in series;

vibrating flow generating means which is equipped to each of said electrolytic tanks and generates vibrating flow in waste liquid to be treated; and

a power supply circuit for applying a voltage between said anode and said cathode,

wherein said vibrating flow generating means comprises vibration generating means; vibration transmitting rods which are operationally connected to said vibration generating means so as to vibrate in the waste liquid to be treated; and vibrating vanes fixed to said vibration transmitting rods.

7. The apparatus for continuously electrolyzing waste liquid as claimed in claim 6, wherein the distance between said anode and said cathode is set to 5 to 50 mm.

8. The apparatus for continuously electrolyzing waste liquid as claimed in claim 6, wherein vibrating stress dispersing means is interposed between said vibration generating means and said vibration transmitting rods and/or between said vibration transmitting rods and said vibration vanes.

9. The apparatus for continuously electrolyzing waste liquid as claimed in claim 6, wherein said vibration generating means is used commonly by plural vibrating flow generating means.

10. The apparatus for continuously electrolyzing waste liquid as claimed in claim 6, wherein plural electrolytic tanks constituting said series of tanks are unified, and said electrolytic tanks thus unified are partitioned by respective partition walls.

11. The apparatus for continuously electrolyzing waste liquid as claimed in claim 10, wherein a chute is equipped between the respective continuous electrolytic tanks thus unified so that the waste liquid to be treated is fed from one electrolytic tank to the other electrolytic tank.

12. The apparatus for continuously electrolyzing waste liquid as claimed in claim 11, wherein said chute is equipped with a flow-in cut-out portion into which the waste liquid to be treated flows from the one electrolytic tank of said continuous electrolytic tanks of the unified electrolytic tanks, and a flow-out cut-out portion from which the, waste liquid to be treated flows out to the other electrolytic tank of said continuous electrolytic tanks of the unified electrolytic tanks.

13. The apparatus for continuously electrolyzing waste liquid as claimed in claim 12, wherein the one electrolytic tank of said continuous electrolytic tanks of the unified electrolytic tanks is equipped with a dam adjacently to said flow-in cut-out portion.

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