(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) Publication number: **0 625 568 A1**

(12) **EUROPEAN PATENT APPLICATION**

(21) Application number: **94107626.7**

(51) Int. Cl.^{5}: **C11D 7/32**, C11D 7/50

(22) Date of filing: **17.05.94**

(30) Priority: **18.05.93 JP 115713/93**
30.08.93 JP 214419/93
06.09.93 JP 221340/93

(43) Date of publication of application:
23.11.94 Bulletin 94/47

(84) Designated Contracting States:
BE DE FR GB IT NL SE

(71) Applicant: **SUMITOMO CHEMICAL COMPANY, LIMITED**
5-33, Kitahama 4-chome
Chuo-ku
Osaka (JP)

(72) Inventor: **Konishi, Shinji**
9-7-203, Kurosuna-3-chome,
Inage-ku
Chiba-shi (JP)
Inventor: **Morimoto, Hitoshi**
2-40, Hirata-1-chome
Ibaraki-shi (JP)

(74) Representative: **VOSSIUS & PARTNER**
Siebertstrasse 4
D-81675 München (DE)

(54) Cleaning solution for apparatuses contacted with quinone diazide photosensitizers and cleaning method using the same.

(57) The present invention provides a cleaning solution excellent in cleaning efficiency which is used for cleaning apparatuses for producing photosensitive agents, apparatuses for preparing positive type resist solutions or spin coater line pipings. The invention further provides a practically useful cleaning method.

The cleaning solution is characterized by containing N-methylpyrrolidone and the cleaning method is carried out using the cleaning solution.

Rank Xerox (UK) Business Services
(3.10/3.09/3.3.4)

The present invention relates to a cleaning solution for apparatuses used for producing quinone diazide photosensitizers, apparatuses used for preparation of positive resist solutions containing the quinone diazide photosensitizers, or spin coater line pipings (apparatuses for coating positive resist solutions used for making integrated circuits, etc.) and a cleaning method using the cleaning solution.

With recent increase in the degree of integration of LSI devices, the design rule of integrated circuits has become finer from about 1 µm to 0.5 µm. Positive resist solutions (comprising an alkali-soluble resin, a quinone diazide photosensitizer and a solvent) used for such fine processing are required to have good basic performances (such as resolution, sensitivity, profile, coatability and depth of focus) and in addition are required to contain less fine particles. That is, when a substrate is subjected to etching using a resist pattern prepared from a positive resist solution containing many fine particles which are visually unobservable, unevenness in coating sometimes occurs in the portions of the substrate which are covered with the resist pattern to cause decrease in the yield in making integrated circuits.

On the other hand, according to the research conducted by the inventors, it has been elucidated that the fine particles result mainly from the quinone diazide photosensitizers (such as 1,2-benzoquinone diazide-4-sulfonate ester, 1,2-naphtoquinone diazide-4-sulfonic ester, 1,2-naphthoquinone diazide-5-sulfonate ester, etc.).

When the kind of quinone diazide photosensitizer to be produced is changed to another kind of quinone diazide photosensitizer, usually a small amount of the photosensitizer previously produced remains in the empty apparatus after the product photosensitizer has been drawn out therefrom. Therefore, the apparatus must be cleaned with a solvent such as acetone before starting of the production of the another photosensitizer. However, only the cleaning with a solvent such as acetone does not necessarily afford a sufficient cleaning efficiency and the fine particles and undesirable components coming from the fine particles remain in the apparatus. Moreover, in preparing a positive resist solution, when the kind of the resist solution to be prepared is changed to another kind of resist solution, a small amount of the resist solution previously prepared remains in the empty apparatus after the resist solution prepared has been drawn out therefrom. Therefore, in this case, before preparation of the new resist solution, the apparatus must be cleaned with solvents such as xylene, amyl acetate, ethyl lactate, γ-butyrolactone, 2-heptanone, propylene glycol monoethyl ether acetate, ethyl cellosolve acetate, etc. However, only the cleaning with a solvent such as ethyl cellosolve acetate does not necessarily afford a sufficient cleaning efficiency and the fine particles or undesirable components coming from the fine particles remain in the apparatus. Likewise, when the kind of the resist solution is changed, a small amount of the previous solution containing the quinone diazide photosensitizer remains in the empty spin coater line piping after the previous resist solution has been discharged. However, good cleaning efficiency for the piping cannot necessarily be obtained with use of solvents such as acetone.

The object of the present invention is to provide a cleaning solution for apparatuses used for producing quinone diazide photosensitizers, apparatuses used for preparing positive resist solutions, and spin coater line pipings, said cleaning solution being excellent in cleaning efficiency, and a cleaning method using the cleaning solution.

According to the present invention, there is provided a cleaning solution for apparatuses used for the production of quinone diazide photosensitizers, apparatuses for the preparation of positive resist solutions or spin coater line pipings, said cleaning solution being characterized by containing N-methylpyrrolidone.

Furthermore, according to the present invention, a method for cleaning the above apparatuses or the above pipings with the above-mentioned cleaning solution is provided.

Fig. 1 is a diagrammatic representation of an apparatus used for producing photosensitizers.

Fig. 2 is a diagrammatic representation of an apparatus used for preparing positive resist solutions.

Fig. 3 is a diagrammatic representation of a spin coater line piping.

Fig. 4 is a diagrammatic representation of a spin coater line piping where the pump and the valve are directly connected.

In Figs. 1-4, the reference numerals denote the following:

(2) --- Reaction vessel
(3a) --- First filter
(3b) --- Second filter
(4) --- Crystallizing vessel
(52) --- Mixing vessel
(53a) --- First filter
(53b) --- Second filter
(54) --- Storage tank
(101) --- Resist solution bottle (or cleaning solvent bottle)

(102) ---	Teflon tube
(103) ---	Bellows type pump
(104) ---	Filter housing
(105) ---	Air operation valve
(106) ---	Quart bottle

When an apparatus used for producing photosensitizers which comprises a reaction vessel, a crystallizing vessel, filters connected through piping to these vessels and pipings connecting these vessels and filters is cleaned with cleaning solutions, the cleaning efficiency is improved in the case of using the cleaning solution containing N-methylpyrrolidone as compared with using a conventional solvent such as acetone or the like. For example, comparison of the results of one cleaning reveals that the amount of the remaining quinone diazide photosensitizer markedly decreases. Furthermore, when an apparatus used for preparation of positive resist solutions which comprises a mixing vessel, a filter connected to the mixing vessel through piping and a piping which connects these mixing vessel and filter is cleaned with the cleaning solutions, the cleaning efficiency is improved in the case of using the cleaning solution containing N-methylpyrrolidone as compared with using a conventional resist solvent such as ethyl cellosolve acetate or the like. For example, when comparison is made on the results of cleaning several times using a given amount of the cleaning solution, the amount of the photosensitizer remaining after cleaning markedly decreases. Likewise, in the case of cleaning a spin coater line piping comprising a resist solution bottle, a Teflon tube, a pump, a filter housing, a valve and a quart bottle, the cleaning efficiency is improved when the cleaning solution containing N-methylpyrrolidone is used, as compared with when a conventional solvent such as acetone is used. For example, much decrease is seen in the amount of the cleaning solution required for the concentration of the quinone diazide photosensitizer in the waste cleaning solution reaching a level of less than 0.01 ppm.

As the method for cleaning the spin coater line piping, mention may be made of, for example, a method which comprises carrying out cleaning with the same solvent as the solvent contained in the resist solution with or without discharging the resist solution from the spin coater line piping and then carrying out cleaning with a cleaning solution containing N-methylpyrrolidone. The generically used solvents contained in the resist solution include glycol ether esters such as ethyl cellosolve acetate, etc. The cleaning is carried out by the means such as stirring, dipping, or passing of the solution.

As the cleaning solutions of the present invention, there may be used N-methylpyrrolidone alone or mixtures of N-methylpyrrolidone with one or more other organic solvents compatible therewith. The organic solvents include, for example, dichloromethane, cyclopentanone, acetone, ethylacetate, γ-butyrolactone, propylene glycol monoethyl ether acetate, ethyl cellosolve acetate and the like.
Especially preferred are dichloromethane, cyclopentanone and acetone.

The mixing ratio in weight is 0-3 parts, preferably 0-1.5 parts of the organic solvent per 1 part of N-methylpyrrolidone.

Next, an example of the present invention is explained in detail referring to the accompanying drawings.

In this example, an apparatus for producing photosensitizers having the construction detailed below is once preliminarily cleaned with acetone as a solvent and then with the cleaning solution of the present invention.

Usually, as shown in Fig. 1, the apparatus for producing photosensitizers comprises mainly a reaction vessel (2) in which a starting solution is charged from stock container (1) by pump (P), a first filter (3a) inserted in the discharging piping from the reaction vessel (2), a crystallizing vessel (4) into which a reaction mixture is introduced, and a second filter (3b) inserted in the discharging piping from the crystallizing vessel (4), and the photosensitizer is produced, for example, through the following steps.

A starting solution (a mixture of 2,3,4,4'-tetrahydroxybenzophenone, 1,2-naphthoquinone diazide-5-sulfonyl chloride and dioxane) is introduced into reaction vessel (2) by pump (P) from stock container (1) and triethylamine is added dropwise to the mixture at room temperature to carry out the reaction in the reaction vessel (2). After completion of the addition, the reaction is allowed to proceed for a while at the same temperature and then the discharging valve (21) at the bottom of the reaction vessel (2) is opened to take out the reaction mixture. The triethylamine hydrochloride which is a by-product formed in the reaction is removed by the first filter (3a). The reaction mixture is introduced into crystallizing vessel (4) in which deionized water is charged. A slurry containing the crystal precipitated in the crystallizing vessel is drawn out from the crystallizing vessel (4) by opening the discharging valve (41) provided at the bottom and filtrated by the second filter (3b) connected to the crystallizing vessel through piping. After completion of the filtration, the photosensitizer in the form of a fine crystal is taken out from the second filter (3b).

In the case of, for example, changing the kind of the photosensitizer to be produced, the whole of the empty apparatus after completion of a series of the above-mentioned steps is cleaned.

Example 1

In the method of this example, a small amount (30 liters) of a mixture of acetone and N-methylpyrrolidone (1:1 in weight ratio) as a cleaning solution is introduced into the stock container (1) and charged in the reaction vessel (2) by the pump (P). The stirrer (22) provided in this reaction vessel (2) is kept under operation for a given time (about 60 minutes) and the reaction vessel is heated whereby the internal surface of the reaction vessel (2) is cleaned by refluxing. The reaction vessel (2) in the apparatus for producing photosensitizer used in this example is a covered cylindrical container having a diameter of about 80 cm and a capacity of 200 liters. Accordingly, the cleaning solution charged in the reaction vessel (2) does not fill the reaction vessel (2) and is stored at a depth of about 1/5 of the total height of the vessel. The vaporized component of the cleaning solution fills the vessel by heating and contacts with a condenser (not shown) provided at the top portion of the reaction vessel (2) to produce a condensation liquid, which flows down along the internal surface of the reaction vessel (2). Therefore, the internal surface of the reaction vessel (2) other than the surface which contacts with the cleaning solution can also be cleaned by stirring for a given time.

In order to ensure the cleaning of the internal surface of the reaction vessel (2) which does not contact with the cleaning solution, such construction may be employed that a shower head (23) is provided at the outlet of the piping extending from the pump (P) in the reaction vessel (2) as shown by the imaginary line in Fig. 1 so that the solution jetted from the shower head can be sprayed at around the upper end portion of the internal surface of the body of the reaction vessel (2). In charging the cleaning solution in the reaction vessel (2), the cleaning solution is jetted in the form of a shower against the internal surface of the body portion of the reaction vessel (2) and as a result, the internal surface of the body portion of the reaction vessel (2) is cleaned during the introduction of the cleaning solution.

After completion of the cleaning of the inside of the reaction vessel (2), the discharging valve (21) is opened and the cleaning solution is allowed to pass through the first filter (3a) and is introduced into crystallizing vessel (4) by the pump (P).

The first filter (3a) comprises a covered container with a filter fabric provided at the bottom and the filtration is carried out by passing the cleaning solution through the filter fabric. Since the filter fabric has a certain resistance against the passing of the cleaning solution, the cleaning solution discharged from the reaction vessel (2) and introduced into the filter is once stored in the space above the filter fabric and thereafter gradually passes through the filter fabric. In the first filter (3a) in this example, the pressure in the space above the filter fabric is the same as the pressure (atmospheric pressure) in the reaction vessel (2).

The cleaning solution which has passed through the filter fabric as aforementioned is introduced into the crystallizing vessel (4) by the pump (P). Since the size of this crystallizing vessel (4) is nearly the same as that of the reaction vessel (2), the depth of the cleaning solution introduced into the crystallizing vessel (4) and stored therein is about 1/5 of the height of the crystallizing vessel (4).

This cleaning solution stored is stirred by stirrer (42) provided in the crystallizing vessel (4) and is maintained at this state for a given period and the crystallizing vessel is cleaned by refluxing as in the case of cleaning of the reaction vessel (2).

In the case of the construction where a shower head (43) is provided at the outlet of the piping extending from the first filter (3a) as in the reaction vessel (2), the same action and effects as in the cleaning of the reaction vessel (2) are obtained.

Thereafter, discharging valve (41) of the crystallizing vessel (4) is opened to discharge the cleaning solution into the second filter (3b) to clean this filter. The cleaning solution which has cleaned the filter is discharged from the bottom of the second filter (3b) into waste container (5).

The second filter (3b) is a filter of the type where a filter fabric is used like the first filter (3a). However, since the second filter functions so that crystals as a product are retained on the filter fabric and the waste solution passes through the filter fabric, the space formed above the filter fabric is pressurized to a certain pressure by nitrogen gas when the photosensitizer is produced. In cleaning, the cleaning solution may be passed under unpressurized state, but the higher cleaning effect is obtained when it is passed under pressurized state as mentioned above.

In this case, the residual crystal previously produced and remaining in the second filter (3b) is effectively liquefied by the above-mentioned cleaning solution, passes through the filter fabric and is discharged from the bottom of the second filter (3b).

The above cleaning steps in a series are effected three times and then, a final finishing cleaning is effected in the same manner. Thus, cleaning of the apparatus for the production of photosensitizer is completed.

In the whole cleaning steps, the cleaning solution which has been used in the first cleaning step is abandoned as it is, but in the third cleaning step the second cleaning solution discharged from the second filter (3b) is reused. Thereafter, a fresh cleaning solution is used in the final cleaning.

In the method of this example, the concentration of the quinone diazide photosensitizer in the waste solution taken out from the second filter (3b) after effecting the first cleaning was about 10,000 ppm. The concentration after the second cleaning with the fresh cleaning solution was about 100 ppm. The concentration of the quinone diazide photosensitizer in the waste solution after effecting the final cleaning decreased to about 0.01 ppm.

When the above apparatus for producing photosensitizer was cleaned in the same manner as above using acetone as the cleaning solution, the concentration of the quinone diazide photosensitizer in the waste solution taken out from the second filter (3b) after effecting the first cleaning was about 1000 ppm and that in the second waste solution was about 10 ppm. It is clear therefrom that the cleaning efficiency of the cleaning solution used in the method of this example is remarkably superior to that of the conventional cleaning solutions.

Example 2

In the above example, the respective cleanings were all carried out with cleaning solutions comprising a mixture of acetone and N-methylpyrrolidone (1:1 in weight ratio), but the first cleaning may be effected with acetone of the conventional cleaning solution.

As aforementioned, acetone is insufficient in the cleaning efficiency. However, since in the first cleaning the cleaning solution is abandoned as it is after cleaning and removal of the quinone diazide photosensitizer, it suffices that a cleaning somewhat inferior to the cleaning with the cleaning solution of Example 1 can be performed.

Therefore, in this Example 2, the first cleaning is carried out with acetone and subsequently, the second and the following cleanings of Example 1 were carried out to obtain nearly the same results as those obtained using the cleaning solution of Example 1 from the first cleaning. In this case, economical cleaning can be effected because acetone is inexpensive.

In the above Example 1, a mixture of acetone and N-methylpyrrolidone (1:1 in weight ratio) was employed as the cleaning solution, but the similar effect can be obtained with a mixture of cyclopentanone and N-methylpyrrolidone (1:1 in weight ratio), a mixture of dichloromethane and N-methylpyrrolidone (1:1 in weight ratio), or the like.

Furthermore, in the cleaning employed in the above examples, the cleaning solution is stored and stirred for a certain time in the reaction vessel (2) and the crystallizing vessel (4). However, in the first cleaning by passing the cleaning solution, a shower head may be used as a connector of the piping to the reaction vessel (2) and the crystallizing vessel (4) and the cleaning solution may be continuously passed through the whole apparatus by allowing the cleaning solution jetted from the shower head to flow down from the upper end portion of the internal surface of the body of the reaction vessel (2) and the crystallizing vessel (4) and discharging it therefrom. It is also possible to employ this method of continuously passing the cleaning solution for the first cleaning and to employ in combination the cleaning by storing and stirring of the cleaning solution for the second and the following cleanings as in the above examples.

Example 3

In this example, an apparatus used for preparing a positive resist solution having the construction detailed below is once cleaned with ethyl cellosolve acetate and then, is cleaned with the cleaning solution of the present invention.

In general, the apparatus for preparing positive resist solution comprises a formulation step part and a bottling step part in combination as shown in Fig. 2. The former formulation step part comprises a mixing vessel (52) in which a mixture of an alkali-soluble resin and a solvent is charged and a positive resist solution is prepared using a photosensitizer and a first filter (53a) inserted in the discharging piping coming from the mixing vessel (52) and the latter bottling step part comprises a storage tank (54) for storing the positive resist solution prepared, a second filter (53b) inserted in the discharging piping coming from the storage tank (54) and a filling machine (60). The positive resist solution is prepared, for example, through the following steps.

A mixture of 1,2-naphthoquinone diazide-5-sulfonate ester of 2,3,4,4'-tetrahydroxybenzophenone (quinone diazide photosensitizer) and m/p-mixed cresol•formaldehyde novolak resin and ethyl cellosolve acetate (solvent) is charged in the mixing vessel (52) and is stirred for a while by stirrer (72) provided therein at room temperature. Thereafter, the discharging valve (71) provided at the bottom of the mixing vessel (52) is opened to take out the positive resist solution prepared. The resulting resist solution is filtrated by the first filter (53a) and the filtrate is stored in the storage tank (54) by the pump (P_3). The first filter (53a) consists of two Teflon filters (80), (80) having a pore diameter of 0.2 µm which are connected in series and the filters are replaceable.

The resist solution introduced into the storage tank (54) is filtrated again by the second filter (53b) having the same construction as the first filter (53a) and is dispensed in resist containers (55), (55) from filling device (60).

In the case of, for example, changing the kind of the positive resist solution to be prepared, the whole of the empty apparatus after completion of the above steps is cleaned.

In the method of this example, the cleaning of the formulation step part from the mixing vessel (52) to the first filter (53a) and the cleaning of the bottling step part from the storage tank (54) to the resist container (55) are effected by the different methods. In the cleaning of the respective step parts, a spray cleaning is carried out so as to improve the cleaning efficiency of the mixing vessel (52) or the storage tank (54). For this purpose, the mixing vessel (52) and the storage tank (54) are provided with spray head (73) and spray head (93) at the part for introduction of the cleaning solution. Furthermore, in order that the whole of the apparatus for preparation can be cleaned by circulation cleaning, a first feedback circuit (74) is provided which returns to the spray head (73) in the mixing vessel (52) from the downstream side of the first filter (53a) and in which pump (P_1) is inserted and in order that the whole of the bottling apparatus can be cleaned by circulation cleaning, a second feedback circuit (94) is provided which returns to the spray head (93) in the storage tank (54) from the downstream side of the second filter (53b) and in which pump (P_2) is inserted. Furthermore, there is provided a discharging pipe (84) in which the first on-off valve (82) is inserted at the end of the downstream of supply piping (81) which supplies the positive type resist solution from the first filter (53a) to the storage tank (54) and in addition, the second on-off valve (83) is inserted in the first feedback circuit at a position near the branching point from the supply piping (81). Moreover, the third on-off valve (85) and the fourth on-off valve (86) are inserted between the first filter (53a) and the pump (P_3).

First, explanation will be given on cleaning of the formulation step part of the apparatus used for preparation of resist solutions constructed as mentioned above.

[Cleaning of the formulation step part]

First to fourth cleanings are conducted for the cleaning of the formulation step part.

The first cleaning is carried out using ethyl cellosolve acetate (solvent). The first cleaning is carried out in the following manner. Under the conditions of the discharging valve (71) provided at the bottom of the mixing vessel (52) being opened and simultaneously therewith the first on-off valve (82) and the third on-off valve (85) being opened, the second on-off valve (83) being closed and the fourth on-off valve (86) being closed, 60 liters of the above-mentioned cleaning solution is introduced into the mixing vessel (52) through the spray head (73). Thus, the internal surface of the mixing vessel (52) is spray cleaned by the cleaning solution shower jetted from the spray head (73) and this cleaning solution is discharged from the discharge pipe (84) of the downstream side through the first filter (53a). In this way, the whole of the apparatus for preparation of resist solution is cleaned by the passing of the cleaning solution. The cleaning solution discharged from the discharging pipe (84) is discarded.

Then, the filter cartridges of the filters (80) in the first filter (53a) are removed. To the cartridges stick a lot of the undissolved photosensitizer in the positive resist solution or fine particles of undesirable components resulting from the components of the undissolved photosensitizer and these cannot be removed by the cleaning. The residual solution in the filters (80) or other portions is drawn out and discarded.

Then, the second cleaning is carried out in the same manner as the first cleaning using the same cleaning solution in the same amount with the filters (80) being closed without mounting the cartridges and the cleaning solution after cleaning is discarded and similarly the residual solution is drawn out and discarded.

Thereafter, the above cleaning by the passing of the cleaning solution is repeated and the primary cleaning is terminated when the content of the photosensitizer in the cleaning solution discharged from the discharging pipe (84) has been reduced to a given level.

The second cleaning:

The second cleaning is carried out using a mixture of acetone and N-methylpyrrolidone (1:1 in weight ratio) as a cleaning solution.

In this cleaning, 60 liters of the above cleaning solution is charged in the mixing vessel (52). This volume of the cleaning solution corresponds to 1/10 of the capacity of the mixing vessel (52).

The discharge valve (71) and the third on-off valve (85) are opened and the first on-off valve (82) is closed and simultaneously the second on-off valve (83) is opened and the fourth on-off valve (86) is closed and the pump (P_1) inserted in the first feedback circuit (74) is kept under operation. This state is continued for 2 hours. Thus, the whole of the path from the mixing vessel (52) to the first filter (53a) is cleaned by circulation and besides, the cleaning solution returning from the first feedback circuit (74) is introduced into the mixing vessel (52) through the first feedback circuit (74) and sprayed to the internal surface of the mixing vessel (52) from the spray head (73). The total amount of the cleaning solution used for this circulation cleaning is set larger than the sum of the capacity of the piping from the mixing vessel (52) to the branching point downstream the first filter (53a) and the capacity of the first feedback circuit (74) and therefore, the inside of the mixing vessel (52) is continuously spray cleaned for the above period of time.

After termination of the circulation cleaning, pump (P_1) is stopped and the cleaning solution in the path of circulation is discharged from the discharging pipe (84) and is discarded.

Then, the second on-off valve (83) is closed and the first on-off valve (82) is opened, and under this state, 120 liters of the same cleaning solution is charged in the mixing vessel (52) to clean the vessel by passing therethrough and the solution is discharged from the discharging pipe (84) and discarded. Furthermore, the residual solution is drawn out.

The third cleaning:

This cleaning is for removal of the cleaning solution used in the above second cleaning and is effected by passing ethyl cellosolve acetate (solvent) as in the first cleaning.

When concentration of the photosensitizer in the cleaning solution discharged from the discharging pipe (84) after one cleaning reaches lower than the set value, the third cleaning is terminated and when it is still higher than the set value, the cleaning is repeated.

By carrying out these first-third cleanings, cleaning of the whole system of the formulation step part is completed. Thereafter, the parts such as filter cartridges and O-rings removed from the filters (80), (80) of the first filter (53a) are cleaned with a mixture of acetone and N-methylpyrrolidone (1:1 in weight ratio) and then with acetone and these are again mounted.

Thus, cleaning of the formulation step part of the apparatus for preparing positive resist solutions is completed.

[Cleaning of bottling step part]

Next, explanation will be given on the cleaning of the apparatus used for the bottling step.

First-third cleanings are also carried out in this cleaning. The first and second cleanings are the same as in the cleaning of the formulation step part, and the cleaning solution is charged in the storage tank (54) through the supply piping (81) under the first on-off valve (82) and the third on-off valve (85) being closed and the second on-off valve (83) and the fourth on-off valve (86) being opened. The second cleaning is a circulation cleaning step (2 hours) where the cleaning solution which has passed through the second filter (53b) is returned to the storage tank (54) through the second feedback circuit (94) by operating the pump (P_2).

In the third cleaning, 60 liters of ethyl cellosolve acetate (solvent) is passed and discarded through the valves and the filling machine (60) provided with filling nozzle (61). Thereafter, 11.2 ℓ of ethyl cellosolve acetate (solvent) is bottled three times using the filling machine (60).

When the number of the fine particles resulting from the photosensitizer in the cleaning solution bottled at the third time is less than the set value, the cleaning is judged to pass and the cleaning is terminated, and the residual solution is drawn out.

When the cleaning is judged not to pass, the bottling is again carried out and the number of the fine particles is checked. This is repeated until the number of the fine particles reaches less than the set value. In case a plurality of the filling nozzles are used in the filling machine (61), the above-mentioned number of bottlings are carried out from each of the filling nozzles and the number of the fine particles in the container in which the cleaning solution is bottled from each filling nozzle is checked.

After completion of the third cleaning, the filling nozzle (61) of the filling machine (60) is removed. This filling nozzle and the parts such as filter cartridges and O-rings which have already been removed from the filters (80) of the second filter (53b) are cleaned with a mixture of acetone and N-methylpyrrolidone (1:1 in weight ratio) and then with acetone.

Thus, cleaning of the apparatus used for bottling step is completed.

According to the investigation, the fine particles are most readily produced in the filling nozzle (61) of the filling machine (60) while according to the present cleaning the filling nozzle (61) of the filling machine (60) is removed and separately cleaned and hence the fine particles which are difficult to remove by the cleaning with passing of the cleaning solution can be surely removed.

In the above Example, the cleaning of the formulation step part and that of the bottling step part in the apparatus for preparation of a resist solution were conducted utterly separately. However, in the second cleaning with a mixture of acetone and N-methylpyrrolidone (1:1 in weight ratio) in the cleaning of the formulation step part, the path from the mixing vessel (52) to the downstream of the second filter (53b) may be cleaned by passing the cleaning solution and thereafter, the step of circulation cleaning which comprises circulating the cleaning solution from the downstream of the second filter (53b) through the second feedback circuit (94), the supply pipe (81) and the first feedback circuit (74) and returning the solution to the mixing vessel (52) may be continued for 2 hours. That is, in this way the bottling part may be also simultaneously cleaned.

Furthermore, the aforementioned first-third cleanings may be carried out for the whole of the apparatus for preparation of resist comprising the formulation step part and the bottling step part, and in some cases, the method for cleaning of the apparatus for preparation of resist according to the present invention can be effected for only one of the two step parts.

In the cleaning of all of the apparatuses or devices in the above Example, the cleaning by the passing of ethyl cellosolve acetate (solvent) followed by discard of the ethyl cellosolve acetate (this cleaning is carried out two or more times), the circulation cleaning with a mixture of acetone and N-methylpyrrolidone and the cleaning for removal of the N-methylpyrrolidone used above are combined. In the case of this combined cleaning, the cleaning efficiency is remarkably improved as compared with using ethyl cellosolve acetate (solvent) as a cleaning solution.

For example, when results of the cleaning of the formulation step part in the above Example which comprises carrying out four times the first cleaning by passing the cleaning solution, then carrying out the second cleaning and thereafter, carrying out the third cleaning are compared with the results obtained by carrying out only the first and second cleanings, the cleaning efficiency of the former cleaning is improved about 10 times over that of the latter cleaning which uses ethyl cellosolve acetate as a cleaning solution if the amount of the cleaning solution and the number of cleaning are the same in each cleaning.

In the above Example 1, a mixture of acetone and N-methylpyrrolidone (1:1 in weight ratio) was used as the cleaning solution, but the same effects are obtained by using a mixture of cyclopentanone and N-methylpyrrolidone (1:1 in weight ratio) or a mixture of dichloromethane and N-methylpyrrolidone (1:1 in weight ratio).

In the above Example, spray cleaning was employed for cleaning of the mixing vessel (52) and the storage tank (54), but other cleaning methods such as refluxing, stirring and dipping can be optionally employed.

Moreover, when the filtration pressure of the first filter (53a) or the second filter (53b) is high, pump (P_0) is inserted in the circuit before these filters as shown in Fig. 2. In this case, if necessary, this pump (P_0) is operated during the cleaning by passing the cleaning solution or the circulation cleaning in each of the above Examples.

Comparative Example 1

The spin coater line piping shown in Fig. 3 was used as a simulative spin coater. In this spin coater piping, a bellows type pump SB-2SH-M manufactured by Iwaki Seisakusho Co., Ltd. was used as the pump, Waferguard WP-16 manufactured by Japan Millipore Co., Ltd. was used as the filter housing part, Waferguard F-16 (pore diameter: 0.2 µm) manufactured by Japan Millipore Co., Ltd. was used as the filter unit, and PDT-SCIMT manufactured by Takasago Seisakusho Co., Ltd. was used as the air operation valve. Teflon tubes were used as the lines connecting these parts and as the discharging nozzle.

After the filter housing part was fitted with the filter, 300 ml of Sumiresist PFI-15 (a positive type resist solution manufactured by Sumitomo Chemical Co., Ltd.) was fed by the pump and filled in the filter housing part and allowed to pass through the filter to carry out filtration of the resist solution. The positive resist solution was filled to reach the discharging nozzle at the end of the spin coater piping by operating the pump. Then, the filter housing part was dismounted and the filter was removed. The filter housing cup was thoroughly cleaned with ethyl cellosolve acetate and the filter housing part was fitted to the spin coater line piping without mounting the filter. Then, ethyl cellosolve acetate was passed by the pump and a waste solution obtained by fractional sampling with every 250 ml was subjected to absorption spectrophotometry at 400 nm. The ethyl cellosolve acetate in an amount of 4250 ml in total was required until the concentration of the quinone diazide photosensitizer in the waste solution reached less than 0.01 ppm.

Comparative Example 2

The same simulative spin coater as used in Comparative Example 1 was used, but after dismounting the filter housing part, the bellows type pump and the air operation valve were directly connected as shown in Fig. 4 and then ethyl cellosolve acetate was passed by the pump and a waste solution obtained by fractional sampling with every 250 ml was subjected to absorption spectrophotometry at 400 nm. The ethyl cellosolve acetate in an amount of 3250 ml in total was required until the concentration of the quinone diazide photosensitizer in the waste solution reached a level of less than 0.01 ppm.

Reference Example 1

Solubilities of the photosensitizer used in Sumiresist PFI-15 manufactured by Sumitomo Chemical Co., Ltd. in some solvents are shown below.

Table 1

Solvent	Solubility
Ethyl cellosolve acetate	36% by weight
N-methylpyrrolidone	50% by weight or higher
Acetone	41% by weight

Example 4

The procedure of Comparative Example 1 was repeated except that a mixture of dichloromethane and N-methylpyrrolidone (weight ratio = 1/1) was passed in place of ethyl cellosolve acetate. 3000 ml of the mixture in total was required until the concentration of the quinone diazide photosensitizer in the waste solution reached a level of less than 0.01 ppm.

Example 5

The procedure of Comparative Example 2 was repeated except that N-methylpyrrolidone was passed in place of ethyl cellosolve acetate. 1750 ml of N-methylpyrolidone in total was required until the concentration of the quinone diazide photosensitizer in the waste solution reached a level of less than 0.01 ppm.

Reference Example 2

A solution containing 10 ppm of the photosensitizer used in Sumiresist PFI-15 in N-methylpyrrolidone was kept at room temperature for 16 hours and absorbance at 400 nm was measured and concentration of the residual photosensitizer was obtained.

Table 2

Time (H)	Absorbance	Content of residual photosensitizer (%)
0	0.212	100%
1	0.152	72%
2	0.125	59%
3	0.116	54%
6	0.102	48%
16	0.100	47%

Claims

1. A cleaning solution for apparatuses used for producing quinone diazide photosensitizers which contains N-methylpyrrolidone.

2. A cleaning solution for apparatuses used for preparing positive resist solutions which contains N-methylpyrrolidone.

3. A cleaning solution for spin coater line pipings which contains N-methylpyrrolidone.

4. A cleaning solution according to any one of claims 1-3 which additionally contains at least one organic solvent selected from the group consisting of dichloromethane, cyclopentanone and acetone.

5. A method for cleaning apparatuses used for producing quinone diazide photosensitizers with using the cleaning solution of claim 1 or 4.

6. A method according to claim 5 which comprises repeating the cleaning two or more times for the whole of the apparatus.

7. A method according to claim 6 which comprises carrying out the first cleaning with acetone.

8. A method according to any one of claims 5-7 which comprises carrying out the cleaning by passing of the cleaning solution, stirring, dipping or refluxing for the main portions of the apparatus other than the piping member.

9. A method for cleaning apparatuses used for preparing positive resist solutions with using the cleaning solution of claim 2 or 4.

10. A method according to claim 9 which comprises repeating the cleaning two or more times.

11. A method according to claim 10 which comprises carrying out the first cleaning with a solvent.

12. A method according to any one of claims 9-11 which comprises carrying out the cleaning of a mixing vessel of the apparatuses by stirring, dipping, spraying or refluxing.

13. A method for cleaning spin coater line pipings which comprises carrying out the cleaning with a solvent with or without discharging the resist solution from the spin coater line pipings and then carrying out the cleaning with the cleaning solution of claim 3 or 4.

14. A method according to claim 13 which comprises carrying out the cleaning by dipping or passing the cleaning solution.

FIG. 1

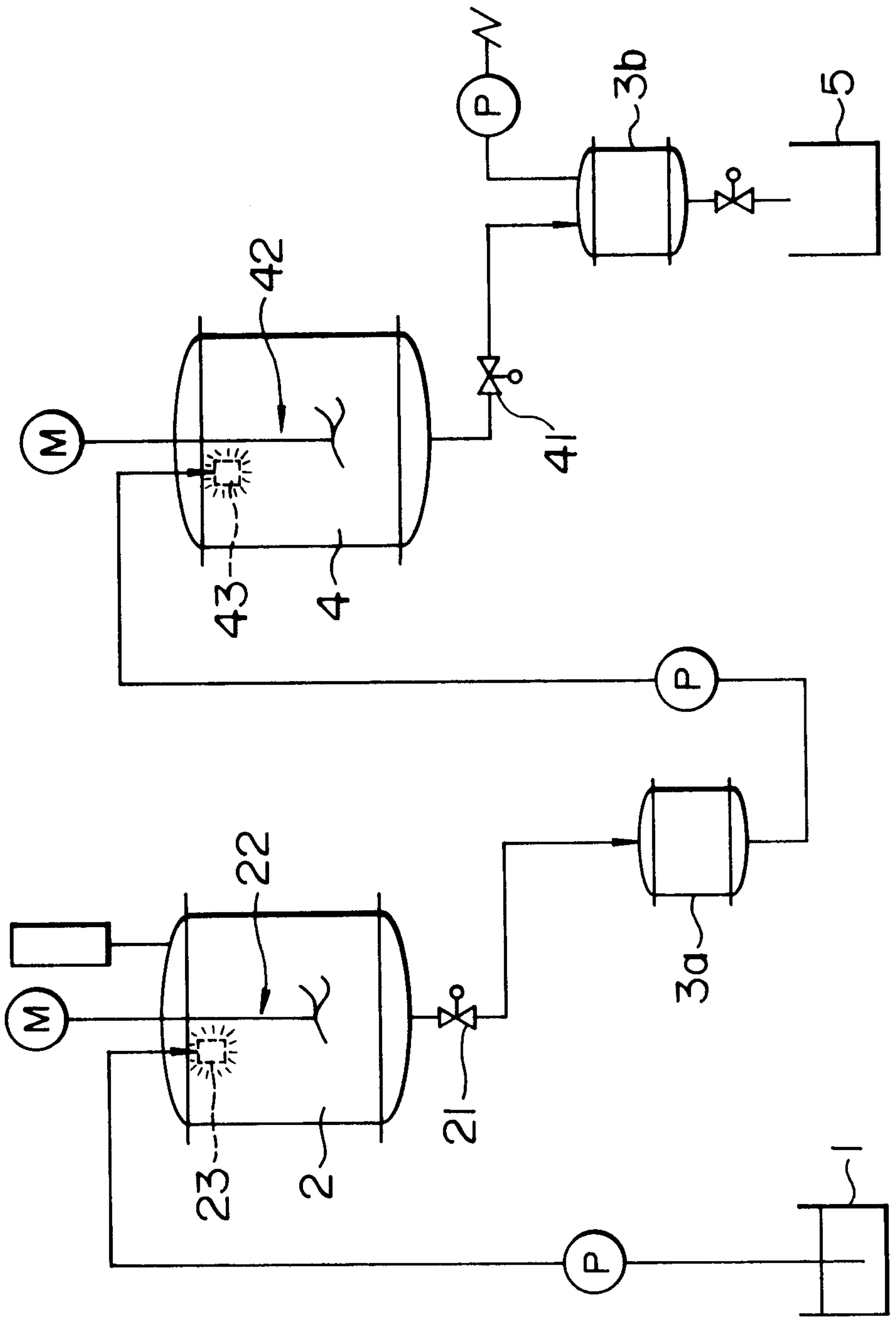
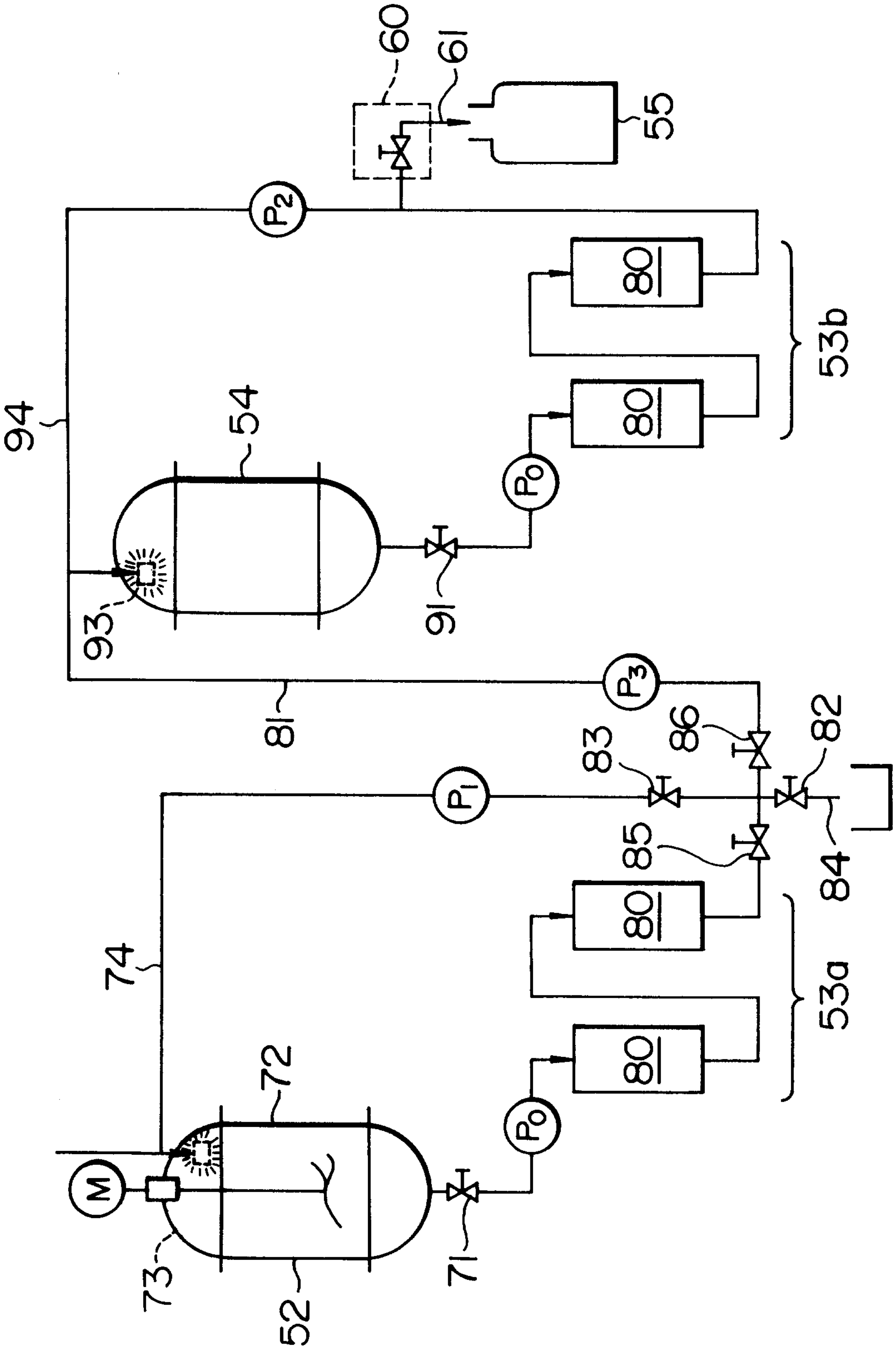


FIG. 2


60
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P2
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FIG. 3

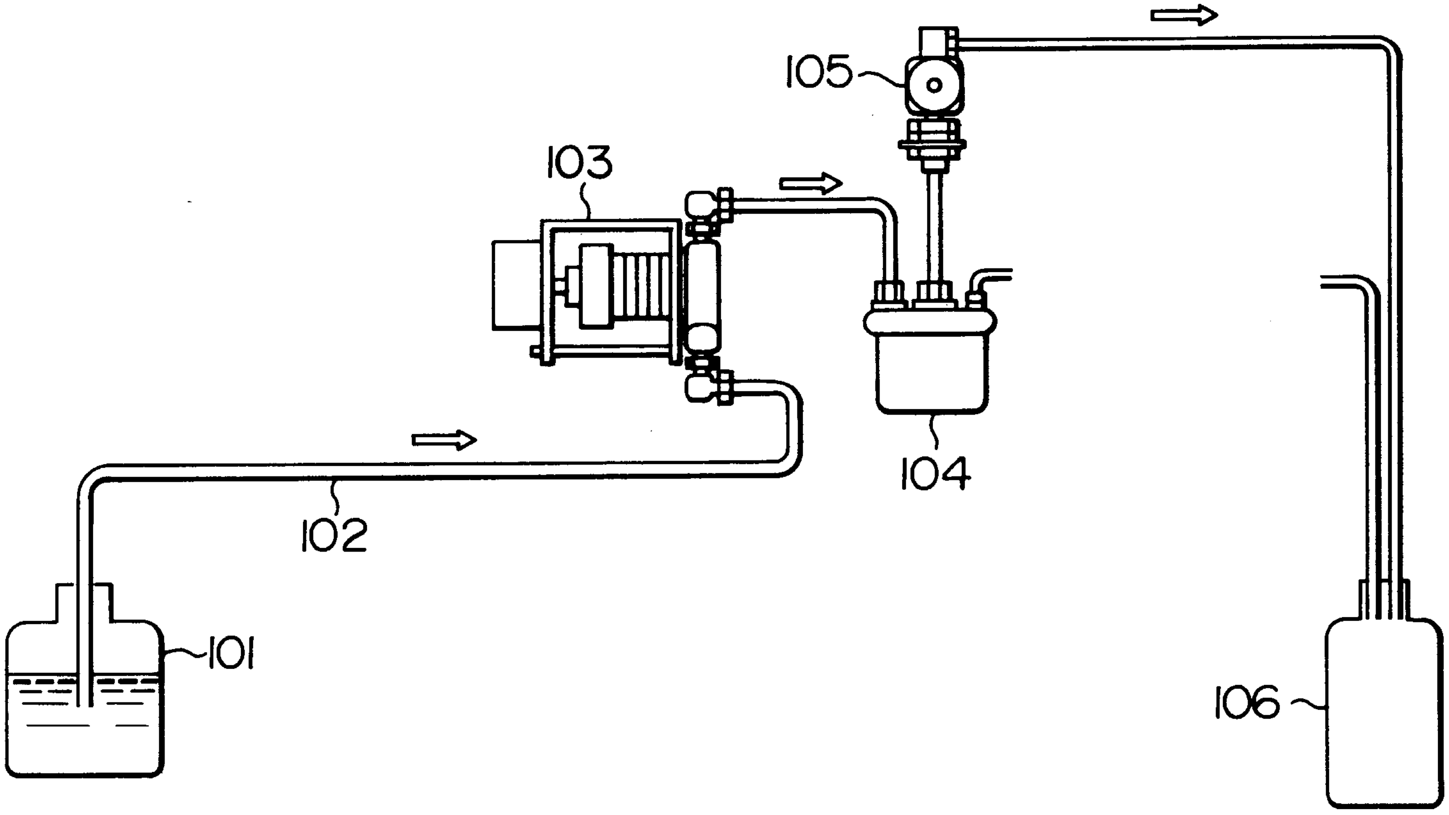
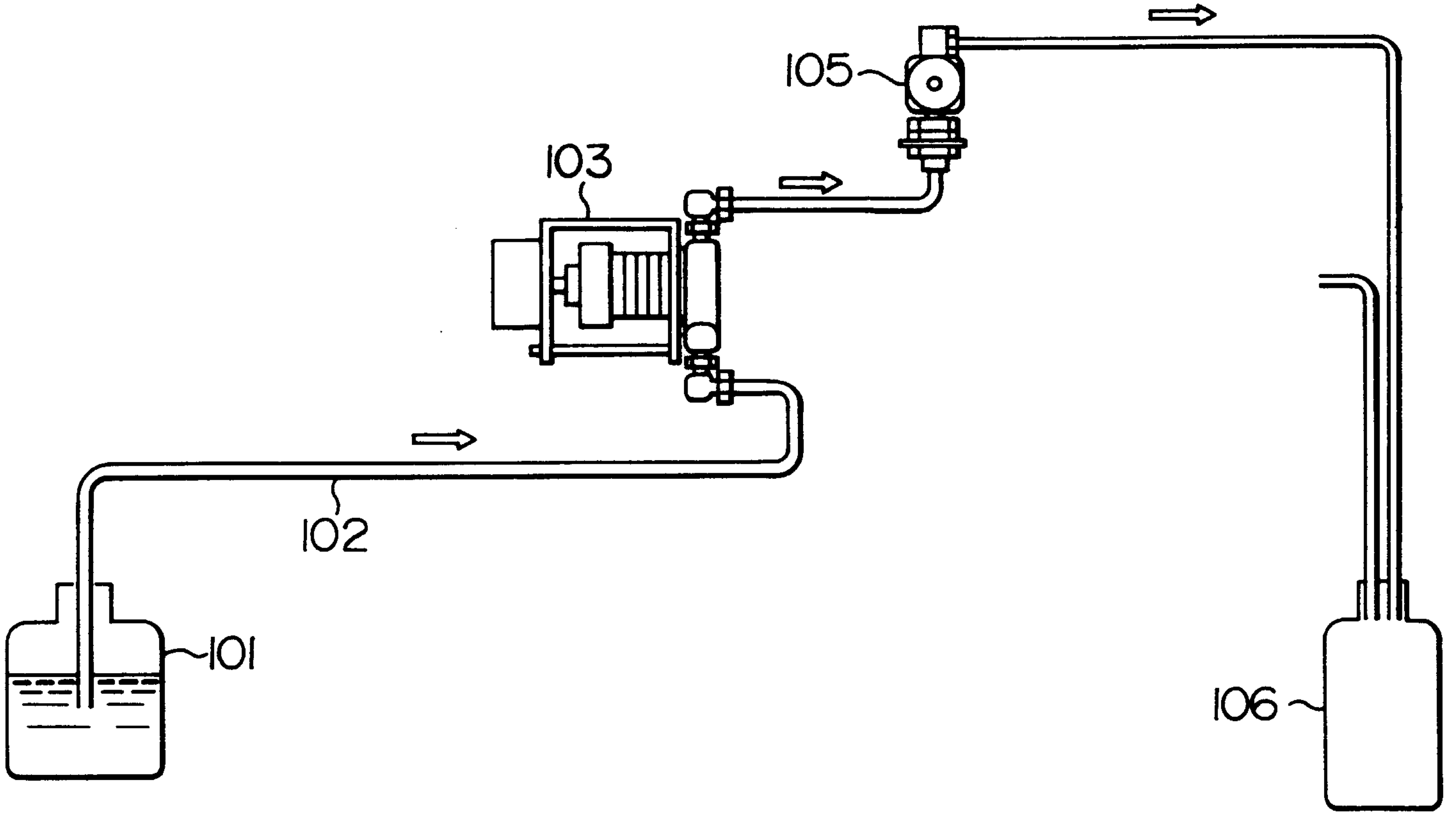


FIG. 4



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EUROPEAN SEARCH REPORT

Application Number
EP 94 10 7626

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.5)
X	DATABASE WPI Week 8601, Derwent Publications Ltd., London, GB; AN 86-005246 & SU-A-1 161 596 (LENINGRAD LENSOVET TECH) 15 June 1985 * abstract * ---	1-4	C11D7/32 C11D7/50
Y	EP-A-0 021 149 (INTERNATIONAL BUSINESS MACHINES CO) * abstract * * page 12, paragraph 2 * ---	1-4	
Y	DATABASE WPI Week 8712, Derwent Publications Ltd., London, GB; AN 87-084322 & JP-A-62 036 663 (MITSUBISHI CHEM IND KK) 17 February 1987 * abstract * ---	1-4	
A	DATABASE WPI Week 9015, Derwent Publications Ltd., London, GB; AN 90-112013 & JP-A-2 063 052 (HITACHI CHEMICAL KK) 2 March 1990 * abstract * ---	1-3	**TECHNICAL FIELDS SEARCHED (Int.Cl.5)** C11D
A	GB-A-2 084 613 (ERNEST IHRINGER) * the whole document * ---	1	
A	GB-A-2 191 501 (PROTECTIVE RESEARCH INDUSTRIES LTD) * claims * ---	1-4	
A	EP-A-0 103 808 (J.T.BAKER CHEMICAL CO) * claims * -----	1	

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
BERLIN	25 August 1994	Pelli Wablat, B

CATEGORY OF CITED DOCUMENTS

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