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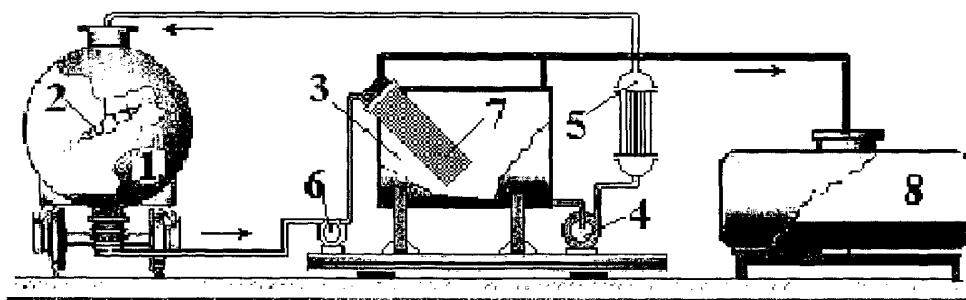
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ance Notes on Codes and Abbreviations" appearing at the begin-
ning of each regular issue of the PCT Gazette.

(54) Title: METHOD OF HYDROCARBON IMPURITIES REMOVAL FROM SURFACES



(57) Abstract: The invention relates to methods of surface cleaning from hydrocarbon impurities such as crude oil, petroleum products, lubricating agents, fats of technical and household grades and oils and can be used in various branches of industry for chemical - and mechanized washing and cleaning of process and transportations means. The technical object of the supposed invention is the simplification of the cleaning process, the increase of hydrocarbon impurities recovery during the regeneration of washing solution and the reduction of power consumption for carrying out the cleaning process. The technical results has been achieved owing to the fact that some changes and modifications have been introduced into the known closed-cycle method of hydrocarbon impurities removal from surfaces which includes the preparation of detergent aqueous solution containing nonionic surfactant and an active component, surface washing-off with detergent aqueous solution, pumping-off of the emulsion obtained, separating of the emulsion into aqueous and organic phases followed by the return of aqueous phase into the cleaning cycle and the periodical discharge of the organic phase to a storage tank.

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Method of Hydrocarbon Impurities Removal from Surfaces

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Field of the Invention

The invention relates to methods of removal of hydrocarbon impurities such as crude oil, petroleum products, lubricating agents, fats of technical and household grades and oils and can be applied in different fields of industry for chemical- and mechanized washing and cleaning of process and transportation means.

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Description of the Prior Art

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The process of treatment (cleaning, washing, degreasing) of equipment, mechanisms, units and parts, as well as vessels and reservoirs contaminated with crude oil, petroleum products, fats and other liquid hydrocarbons is one of the most urgent problems both from the point of view of the working, environmental and fire safety and financial expenditures.

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Previously applied known treatment methods do not now meet modern requirements. The cause of it is the complexity and the incomplete previous study of physico-chemical processes taking place while liquid hydrocarbons removing from surfaces the results of which are influenced by different factors, i.e. surface material, chemical composition and properties of impurities, cleaning process parameters and conditions,

composition of technical detergents, peculiarities of detergents interaction with impurities and so on.

Some methods and compositions as well as various solvents are known and widely used in industry, to clean metal surfaces of oil-, mud-, crude oil- and asphalt- and pitchy 5 impurities. As a rule, universal solvents are used which can dissolve various substances contained in such impurities as acetone, kerosene, white spirit and so on (B.G. Petrik, P.V. Choukov and S.I. Kalashnikov "Handbook: Solvents and compositions for cleaning machines and mechanisms", Moscow, "Khimia", 1989). Main operations included in these methods are washing of surfaces to be treated, pumping-off of formed emulsion of solvent 10 and liquid hydrocarbons and its removal followed by discharging into treatment facilities.

High fire hazard and ecological harmfulness for the environment and attending personnel are the main drawbacks of various liquid solvents used as detergents. Known solvents of high ignition temperature (trichloroethane, trichloroethylene and others) though reducing flammability are extremely toxic and dangerous for attending personnel's health 15 and therefore require very strict observance of safety measures.

The method of petroleum products removal from surfaces is known (USSR, Author's certificate No 944685) which consists in surface cleaning with the aqueous solution of detergents based on surfactants and electrolytes which forms stable emulsion with hydrocarbon impurities. To clean a surface using a closed-cycle method, washing 20 solution is regenerated by the phase separation of emulsion with the help of the electric flotation followed by the removal of organic phase and the return of water suspension into the cleaning cycle.

The above-mentioned method ensures the required level of surface cleaning and the possibility to repeatedly use washing solutions, still the technological process is complicated 25 owing to the formation of stable emulsion which needs either long-time settling or the additional separation by any other method.

The method is known of hydrocarbon impurities removal from surfaces, particularly of oil- and fat contaminants (RU, No 2019318) with the use of two liquids. Washing of an article surface in conformity with this method is performed with washing solution, but 30 impurities are removed from the washing solution with the help of auxiliary liquid which does not form stable emulsion with washing solution and additionally can selectively recover oil- and fat contaminants from it. When the washing procedure is over the auxiliary liquid is regenerated particularly by distillation and returned into the washing cycle.

This method has drawbacks, i.e.: using two liquids what complicates the flow sheet, requires an additional equipment and thus increases expenditures for surface cleaning.

Methods are known of crude oil impurities removal from surfaces with the help of coagulants and various depressing agents, i.e. additives containing hydrocarbon solvent and
5 polymers (RU, No 2109583) or hydrocarbon aqueous suspension and nitrogen, phosphorus and potassium salts (RU, No 2104103) followed by washing of an internal surface with hot water or live steam.

These methods have drawbacks, i.e. the high process temperature (up to 95-100°C) what increases power consumption and bulkiness of the cleaning process equipment.

10 The method described in RU, No 2135304 is the closest to the one offered. Its essence consists in the following: a surface contaminated with various hydrocarbon impurities is washed with detergent aqueous solution capable of emulsifying hydrocarbon impurities. The washing solution is then regenerated with the help of the emulsion phase separation followed by the organic phase separation and the water phase returning to the
15 cleaning cycle. The "UBON" technical detergent (RU, No 2101337) or "BOK" detergent (RU, No 2132367) are used as washing solutions forming non-stable emulsions with hydrocarbon impurities.

The above-mentioned "UBON" detergent has the following composition,
% ww: sodium salt of polyacrylic acid modified by ether groups - 0.1 - 10; electrolyte - 0.5
20 - 40; water - up to 100.

The "BOK" detergent has the following composition, % ww: nonionic surfactant - 0.2 - 14; polyelectrolyte - 2.5 - 5.5; an active additive - the rest. Acrylic acid polymers are used as polyelectrolyte in the said compound, e.g. sodium salt of carboxymethyl cellulose (Na-CMC) and sodium carbonate or sodium carbonate combined with sodium carbamide
25 and / or metasilicate as an active additive. Neonol or synthanol are used as nonionic surfactants in the said detergent composition.

To eliminate organic impurities penetrating into washing solution, the emulsion phase separation is performed in a separation vessel and the water phase to be returned into the washing cycle is passed through an intermediate reservoir. Water phase is taken from
30 the bottom part of the separation vessel and supplied to the cleaning cycle from the bottom part of the intermediate reservoir. During the process of the emulsion phase separation a volume ratio of organic impurities and washing solution is provided for not less than 1 : 2.

The said method ensures the required level of surface cleaning and the possibility to repeatedly use washing solution, still a desired result is achieved by the flow sheet complication as separate stages of the process take place in intermediate vessels but the provision for a volume ratio of impurities and washing solution requires the evaluation of a volume of impurities to be removed before the beginning of a surface cleaning process. Such an evaluation is rather difficult to be done accurately.

When using the "BOK" technical detergent as washing solution it is necessary to take into account that neonol and synthanol belong to nonionic surfactants causing heavy foam formation and while preparing washing solution at relatively low temperatures they can decompose losing their properties. Using metasilicates in washing solution is also undesirable as they can be a cause of a tank internal surface corrosion.

Polyelectrolytes tend to form polymer-colloid complexes what can cause the reduction of organic compound recovery and washing solution purification level.

Brief Summary of the Invention

The technical object of the supposed invention is the simplification of the technological process of cleaning, the increase of hydrocarbon impurities recovery during the washing solution regeneration and the reduction of power consumption for the cleaning process.

The technical object is achieved owing to the fact that some changes and modifications have been introduced into the known closed-cycle method of hydrocarbon impurities removal from surfaces which includes the preparation of detergent aqueous solution containing nonionic surfactant and an active component, surface washing-off with detergent aqueous solution, pumping-off of the obtained emulsion, separating of the emulsion into aqueous and organic phases followed by the return of the aqueous phase into the cleaning cycle and the periodical discharging of the organic phase to a storage tank.

The role of nonionic surfactant is played by a nonionic surfactant based on fatty alcohol alcoxylate in quantity 2 - 4 % ww and an active component in quantity up to 100 %.

The separation of emulsion to be pumped-off into water- and organic phases is carried out by passing it through a self-cleaning thin-layer settler (separator).

The role of fatty alcohol alcoxylate is played by oxyethylated polyoxypropylene glycol derivatives of ethylene diamide or oxyethylated polypropylene ethylene diamine

known under trademarks "Alcatronic EDP, EGE, PGP" and others possessing a number of useful properties including emulsifying and thickening characteristics.

As an active component of a detergent, soda ash is used or a compound with a partial soda ash replacement by phosphoric acid sodium salts, the component weight ratio being equal to 1.9 - 2.3 : 1.

As phosphoric acid sodium salts, tripolyphosphate or trisodiumphosphate or their mixture are used.

Depending upon an impurity type (crude oil, fats, oil) and material of a surface to be cleaned (steel, aluminium or other non-ferrous metals) aqueous washing solution is used with a fluctuating content of detergent, i.e. from 1.5 to 4.0 % ww; washing solution temperature is selected within the limits of 40 - 55°C.

The whole complex of characteristics allows to achieve a number of advantages in comparison with known technical decisions, namely:

- to increase the level of hydrocarbon compounds recovery from contaminated washing solution up to 97 - 98.5 %;
- to reduce power consumption owing to the reduction of washing solution temperature in the course of the cleaning process;
- to improve the environment quality and attending personnel's working conditions owing to the elimination of harmful and hazardous components from detergent composition;
- to reduce cost and time of hydrocarbon impurities removal from an actual area unit at the expense of the efficiency of the detergent composition offered.

Brief Description of the Several Views of the Drawings

Fig. 1 represents a flow diagram of hydrocarbon impurities removal from a surface using the example of a railway tank cleaning.

Description of the Preferred Embodiment of the Invention

The method of hydrocarbon impurities removal from a surface includes the following sequence of operations:

- 5 • the preparation of washing solution of a predetermined concentration on the basis of detergent of the composition selected;
- warming and supplying washing solution for washing-off of a contaminated surface;
- pumping- off the contaminated washing solution (emulsion) into a vessel with
10 washing solution having preliminary passed it through a self-cleaning thin-layer settler;
- discharging an organic phase from the self-cleaning thin-layer settler to a tank containing separated petroleum product;
- removing sludge from the self-cleaning thin-layer settler;
- 15 • if the washing solution is repeatedly used its alkalinity should be controlled and if its concentration fluctuates from a predetermined one it is adjusted by adding water and detergent.

The composition of a detergent to be prepared is determined proceeding from a number of factors, i.e. impurity composition, material from which a tank or other vessel
20 are made, impurity age and so on.

The use of nonionic surfactant based on fatty alcohol alcoxylate as nonionic hydrophilic surfactant is substantiated with the fact that it is well dissolved in water and distinguished with low foam formation in neutral and alkaline media. Besides, it possesses high surface- and interphase activity in an alkaline medium and good wetting properties on
25 a polar and a hard surface and has emulsifying and thickening characteristics as well.

The selection of such a quantitative composition is explained with the fact that if nonionic surfactant content is less than 2.0 % ww the cleaning process indices are reduced as hydrocarbon impurities detachment from a surface to be cleaned becomes difficult and the cleaning rate becomes slower; if nonionic surfactant content is more than 4.0 % ww
30 financial expenditures for cleaning are increased what is inexpedient as cleaning process cost grows.

Soda ash is most often used as an active component as it is the cheapest and wide-spread detergent though its efficiency is somewhat less than the efficiency of more expensive detergents, e.g. tripolyphosphate and trisodiumphosphate. Still, in those cases when hydrocarbon impurities, especially inveterate ones have very complex composition or a surface is very contaminated, a more efficient detergent is worth while to be used. Such a necessity may arise if soda ash or time are deficient and sodium salts of phosphoric acid being available.

The experience has shown that to achieve optimum indices of cleaning it is enough to replace approximately 30 % soda ash, i.e. the ratio "soda ash : sodium salt of phosphoric acid" should be within the limits of 1.9 - 2.3 : 1. If the ratio is more the cleaning quality may not be achieved; if the ratio is less the cleaning process cost price grows.

The range of the admissible concentration of washing solution equal to 1.5 - 4.0 % ww is selected on the basis of the study carried out with the use of washing solutions obtained from the said compositions to remove liquid hydrocarbons from surfaces. It was found that if a tank is made of non-ferrous metal e.g. aluminium it is better to use detergent aqueous solution of 1.5 - 2.5 % concentration, but if a surface is made of steel or cast iron it is better to use detergent aqueous solution of 2.0 - 4 % concentration.

If the concentration of washing solution is smaller time of the cleaning process increases, if the concentration is higher cleaning expenditures increase.

After a predetermined composition of detergent has been selected and diluted to a predetermined concentration (the preparation of washing solution can be carried out in a separate vessel or directly in vessel 3) pressure pump 4 conveys it through heat exchanger 5 to washing heads 2 installed in tank 1. Washing solution warming up to 40 - 55°C is performed in heat exchanger 5. Concrete temperature is selected proceeding from the detergent composition, solution concentration and optimum cleaning time. At temperatures lower than 40°C the cleaning process time is significantly increased but at temperature higher than 55°C the cleaning process efficiency is reduced as foam formation increases what makes difficult the process equipment operation; nonionic surfactant activity drops. Owing to washing heads of a turbine type an internal surface of a vessel to be cleaned is washed by the spray washing method. To achieve maximum efficiency, washing heads are arranged so that their orientation could be changed if necessary. Average washing time is 8 - 20 minutes.

Spent washing solution is with the help of diaphragm pump 6 supplied to the self-cleaning thin-layer settler 7 where liquid phase is separated into washing solution which, while being cleaned, is fed to vessel 3 for the subsequent use, and into lighter phase, i.e. hydrocarbon impurities which are accumulated in the upper zone of separator 7 and as far as they are accumulated they are pumped into storage vessel 8 for decanted product; sludge is accumulated in the lower, stagnant zone of the separator.

The self-cleaning thin-layer settler is a coalescing separator in the casing of which a plane-parallel packing is installed. Self-cleaning of the packing is achieved by the selection of the treatment modes, as well as of appropriate slope of plates which depends upon the composition and properties of the mixture to be separated. A slot gap between plates is provided owing to packings. A mixture to be separated (emulsion) is supplied into the gap through an upper branch pipe and distributed among slot channels which have three areas, i.e. a vertical area where the separation of petroleum product particles takes place at the plate walls; a rotary area where the flow changes its orientation in the gravitational field and an expanding area where the separated organic phase floats up to the upper part of the apparatus and is discharged into the decanted petroleum product tank. Settled sludge is removed through the bottom branch pipe of the self-cleaning thin-layer settler.

In comparison with the best foreign analogues, e.g. the analogue developed by the company Utility Vault Co, the self-cleaning thin-layer settler does not require frequent stops and dismantling to clean and regenerate the plane-parallel packing. In comparison with settlers equipped with a crimped packing "Quantek" with 45° slope the above-mentioned settler ensures any slope of plates and does not require repeated agitating of separated phases.

In the course of the repeated use of washing solution its concentration is controlled according to an alkalinity value with the help of hydrochloric acid titration using methyl orange indicator and if necessary it is adjusted by adding water and detergent into vessel 3. The dependence of washing solution total alkalinity upon its concentration is shown in Table 1.

Table 1

Washing solution concentration, % ww	Solution density at 20°C, g/cm ³	Total alkalinity of washing solution, %
1.5	1.012	1.3

2.0	1.018	1.6
2.5	1.024	2.0
3.0	1.029	2.6
3.5	1.034	3.1
4.0	1.0385	3.7

Usually the solution adjustment is carried out in 6 - 8 cycles of the cleaning process by adding freshly-prepared washing solution in a quantity sufficient to bring the total concentration of the solution to a predetermined value.

5 In conformity with the flow sheet shown in Fig. 1 it is possible to wash railway tanks and tank trucks, vertical, horizontal and underground stationary reservoirs, as well as other vessels for storage and transportation of liquid hydrocarbons. Concrete examples of the method implementation are given below.

10 Example 1: Washing of a steel tank, 63 m³, was performed with 3.5 % solution of detergent (35 kg of detergent per 1000 liter of water) of the following composition: 3.0 % ww nonionic surfactant representing oxyethylated polyoxypropylene glycol derivative of ethyldiamine (Alcatronic EDP) and 97 % ww soda ash.

The said washing solution was from reservoir 3 (Fig. 1) taken for washing from the
 15 reservoir bottom flange with the help of ejector pump 4 and supplied to washing heads 2 installed inside the tank, each of the heads having two nozzles. Pressure of washing liquid was 1.5 MPa. Washing solution temperature was controlled with the help of a thermometer and maintained within the range of 45 - 55°C owing to its warming by heater
 5. After 10 minutes of spray washing the obtained emulsion representing the mixture of
 20 washing solution and liquid hydrocarbons was pumped off with the help of diaphragm pump 6. Contaminated washing solution was supplied to the upper part (a branch pipe) of the self-cleaning thin-layer settler 7. The passage of emulsion representing the mixture of washing solution and liquid hydrocarbons through the self-cleaning thin-layer settler allowed to remove the basic volume of impurities at this stage and thus to practically eliminate
 25 the stage of the gravitational settling of contaminated washing solution. Cleaned washing solution was directed via the upper branch pipe to the reservoir 3 containing washing solution. Time of phase separation was only several minutes.

Organic phase floated up into the upper part of the settler 7 and was removed with the help of a pump or special fat catchers into the storage tank of decanted product 8. Such a separation of emulsion resulted in 98.5 % recovery of liquid hydrocarbons in comparison with 95 % for the prototype.

5 Periodically samples were taken through the sampler installed at the line of washing solution supply (not shown in Fig. 1) and total alkalinity of the solution was checked.

In Example 1 approximately 30 liter of water and 800g of detergent were added after eight washing cycles for the adjustment of the concentration predetermined.

Example 2 : Washing of the similar railway tank was performed, but detergent
10 composition was changed by the partial replacement of soda ash with sodium salt of phosphoric acid. The detergent had the following composition, % ww: nonionic surfactant - 3.0; tripolyphosphate - 30 and soda ash - the rest to 100. Washing solution concentration was 3.5 % as in Example 1. The washing process was carried out similar to one described in Example 1, but time of the tank washing reduced to 7.5 minutes.

15 The level of hydrocarbons recovery from emulsion was 98 %.

Example 3: Cleaning of a brass reservoir, 5 m³, of machine oil drain residues was performed. 20 kg of detergent having composition corresponding to Example 1 were dissolved in 1000 liter of water at 45°C while permanently agitating. The reservoir cleaning was performed similarly to one described in Example 1.

20 Washing time was 6 minutes, the level of hydrocarbons recovery was 97.5 %.

Example 4: Cleaning of a reservoir similar to one represented in Example 3 was performed but the detergent had the following composition, % ww: nonionic surfactant based on oxyethylated polypropylene ethylene diamine as fatty alcohol alcoxylate - 3.0; trisodiumphosphate - 20.0; tripolyphosphate - 12.0 and the rest was soda ash - to 100.
25 Concentration of the said detergent aqueous solution was 2 % as in Example 3.

Washing time was 5 minutes, the level of hydrocarbons recovery (machine oil) was 98.5 %.

The method was approved with respect not only to railway tanks, but to other articles. Thus, Table 2 gives data concerning cleaning reservoirs for petroleum product
30 storage and Table 3 gives data concerning cleaning vertical cylindrical reservoirs of different volumes installed under a panel roof. Washing solutions containing 3 - 4 % of detergents were used.

Table 2

Reservoir	Internal diameter, m	Length, m	Actual volume, m ³	Internal surface area, m ²	Losses of technical detergent, kg	Mean time of washing off, min
PC-25	2.0	8.3	20.8	58.4	0.3	6
PC-50	2.4	11.3	41.5	94.9	0.5	10
PC-100	3.0	14.6	82.6	140.7	0.7	14
PC-160	3.4	18.5	133.0	200.4	1.0	20
PC-200	3.4	22.9	166.0	262.7	1.3	26
BC-50	2.4	11.5	41.0	96.4	0.5	10
BC-100	3.0	14.6	82.6	151.6	0.8	15
BC-160	3.4	18.2	133.0	198.3	1.0	20
BC-200	3.4	22.6	166.0	259.5	1.3	26

Table 3

5

Reservoir	Internal diameter, m	Height, m	Actual volume, m ³	Internal surface area, m ²	Losses of technical detergent, kg	Mean time of washing off, min
PBC-200	6.6	5.9	204	177.7	0.9	18
PBC-300	7.5	7.3	332	264.7	1.3	25
PBC-400	8.5	7.3	421	313.7	1.6	30
PBC-700	10.4	8.8	757	457.0	2.3	45
PBC-1000	12.3	8.8	1056	581.0	2.9	60
PBC-2000	15.2	11.8	2135	924.9	4.6	90

On the average, when using a detergent containing the similar quantity of nonionic surfactant and different active components (only soda ash or its partial replacement with sodium salts of phosphoric acid) time of washing differs by 8-12 %. To keep time of washing unchanged, the washing solution concentration should be reduced by 0.10-0.18 % ww. Hydrocarbon recovery is 97.5-98.5 %.

10

It is possible to make a conclusion that the efficiency of the use of self-cleaning thin-layer settlers is increased owing to the fact that an electrostatic charge of contaminated solution does not arise as a result of the use of washing solution of the said composition. It is practically neutral, therefore the organic phase is pressed to plates and spread all over their surfaces increasing the level of separation from the contaminated solution.

Thus, in comparison with known methods of hydrocarbon removal from surfaces and compositions of a detergent being used for these purposes the proposed method has several advantages, namely:

- the increase of hydrocarbons recovery from contaminated washing solution up to 97 - 98.5 %;
- the reduction of power consumption owing to the washing solution temperature reduction in the course of the cleaning process;
- the elimination of the use of more expensive detergents which additionally contain sodium salts of polyacrylic acid and corrosion inhibitor;
- the improvement of the environment and of attending personnel working conditions owing to the elimination of the above-mentioned components;
- the reduction of cost and time of hydrocarbon impurities removal from a unit of an actual area.

Industrial Applicability

The method may be used in various branches of industry particularly in shipbuilding, transport, petroleum producing- and refining industry where the necessity exists to wash storage vessels and transport liquid hydrocarbons.

We claim :

1. A closed-cycle method of hydrocarbon impurities removal from surfaces including the preparation of detergent aqueous solution containing nonionic surfactant and an active component, the surface washing-off with detergent aqueous solution, pumping-off the obtained emulsion, separating the emulsion into aqueous and organic phases followed by the return of the aqueous phase into the cleaning cycle and the periodical discharge of the organic phase into a tank wherein the role of the nonionic surfactants is played by a nonionic surfactant based on fatty alcohol alcoxylate in quantity of 2.0 - 4.0 % ww and an active component in quantity up to 100 % ww and the separation of the emulsion to be pumped-off into aqueous and organic phases is performed by the emulsion passing through a self-cleaning thin-layer settler.

2. A method as claimed in claim 1 wherein oxyethylated polyoxypropylene glycol derivatives of ethylene diamide or oxyethylated polypropylene ethylene diamine are used.

3. A method as claimed in any of claims 1 and 2 wherein soda ash is used as a detergent active component.

4. A method as claimed in any of claims 1 and 2 wherein the composition containing soda ash and sodium salt of phosphoric acid is used, the component weight ratio being 1.9 - 2.3 :1.

5. A method as claimed in any of claims 1, 2 and 4 wherein tripolyphosphate and / or trisodiumphosphate are used as sodium salts of phosphoric acid.

6. A method as claimed in any of claims 1 - 5 wherein aqueous washing solution is used for washing, the detergent concentration being within the range of 1.5 - 4 % ww and temperature within the range of 40 - 55°C.

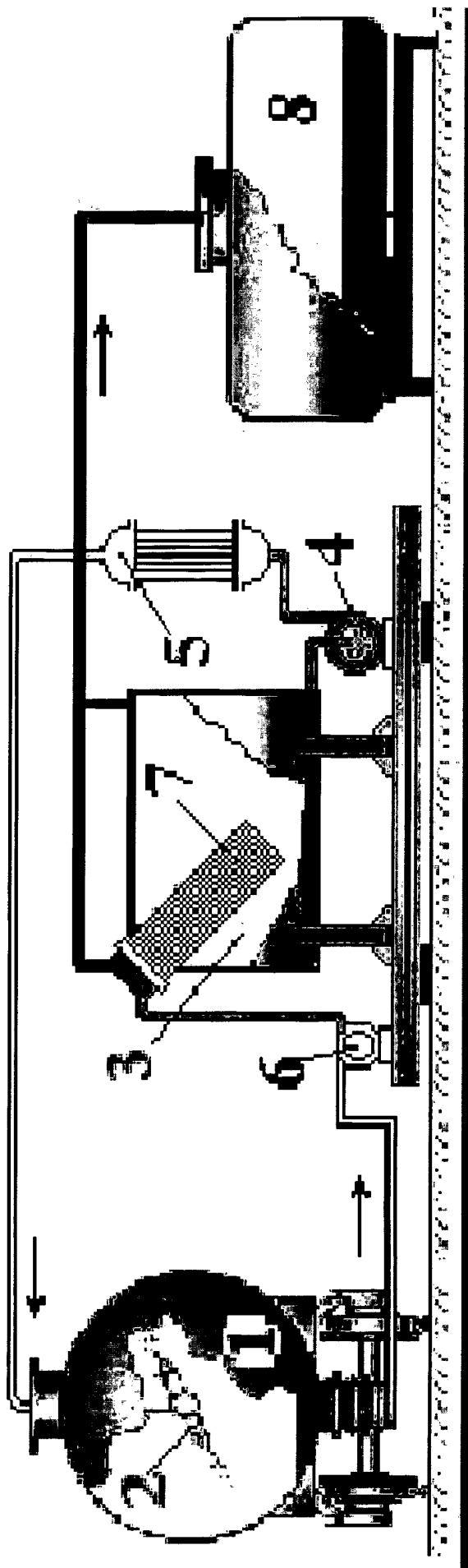


Fig. 1

INTERNATIONAL SEARCH REPORT

International Application No
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A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C11D11/00 C11D1/72 C11D1/722 C11D3/12 B08B3/08
C23G1/00

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED
Minimum documentation searched (classification system followed by classification symbols)
IPC 7 B08B C23G C11D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)
EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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A	<p>US 5 609 693 A (DOBREZ JOHN F ET AL) 11 March 1997 (1997-03-11) claims 1-14</p>	1
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Further documents are listed in the continuation of box C.

Patent family members are listed in annex.

* Special categories of cited documents :

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Date of the actual completion of the international search
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INTERNATIONAL SEARCH REPORT

Inter national Application No

PCT/RU 01/00468

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

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