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Automatic Monitoring and Control of Cleaning Baths

The invention relates to a method of automatically monitoring and controlling cleaning baths, in particular cleaning baths in the metal-processing industry or in vehicle construction. The essence of the invention

5 consists in that at least two selected control parameters are analyzed automatically and in program-controlled manner and the results of the analyses and/or data derived from the results of the analyses are transmitted to a remote destination situated in the direct vicinity of the cleaning
10 bath. Depending upon the result of the analyses, further analyses and/or bath treatment measures can be initiated in program-controlled manner or in response to requests from the remote destination. Additionally, depending upon the result of the analyses, control measurements can be
15 initiated in program-controlled manner or upon request. Here the remote destination can be situated for example in a superordinate process control system, in a control centre of the plant in which the cleaning bath is situated, or at a location outside the plant.

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The cleaning of metal parts prior to their further processing constitutes a standard task in the metal-processing industry. The metal components can be contaminated for example with pigment dirt, dust, metal
25 rubbings, corrosion protection oils, cooling lubricants or deformation agents. Prior to the further processing, such as in particular prior to a corrosion protection treatment (for example phosphation, chromatization, anodization, reaction with complex fluorides etc.) or prior to
30 lacquering, these impurities must be removed by means of a suitable cleaning solution. Spraying, dipping or combined processes can be used for this purpose.

Industrial cleaners in the metal-processing industry are generally alkaline (pH-values in the range above 7, for example 9 to 12). Their basic constituents are alkalis (alkalhydroxides, -carbonates, -silicates, -phosphates, 5 -borates) as well as non-ionic and/or anionic surfactants. As additional auxiliary constituents the cleaners frequently contain complex-forming agents (gluconates, polyphosphates, salts of amino acids such as for example ethylenediamine tetraacetate or nitrilotriacetate, salts of 10 phosphonic acids such as for example salts of hydroxyethane diphosphonic acid, phosphono-butane tricarboxylic acid or other phosphonic- or phosphonocarboxylic acids), corrosion protection means such as for example salts of carboxylic acids with 6 to 12 C-atoms, alkanolamines and foam 15 inhibitors such as for example alkoxyates or alcohols having closed end groups and with 6 to 16 C-atoms in the alkyl group. If the cleaning baths contain no anionic surfactants, cationic surfactants can also be used.

20 As non-ionic surfactants, the cleaners generally contain ethoxylates, propoxylates and/or ethoxylates/propoxylates of alcohols or alkylamines with 6 to 16 C-atoms in the alkyl group, which can also have closed end groups. Alkylsulfates and alkylsulfonates are widely used as 25 anionic surfactants. Alkylbenzene sulfonates are also encountered, although these are disadvantageous from the environmental standpoint. In particular, cationic alkylammonium compounds having at least one alkyl group with 8 or more C-atoms are suitable as cationic 30 surfactants.

The alkalis in the cleaning bath contribute to its cleaning capability. For example, they saponify saponifiable impurities, such as for example fats, and thus render these 35 water-soluble. They also contribute to the removal of insoluble dirt particles from the metal surface in that they negatively charge the surfaces by adsorption of OH-

ions and thus effect an electrostatic repulsion. As a result of such reactions, and possibly also dragging-out, alkalinity is exhausted so that the cleaning effect diminishes over time. Therefore conventionally the

5 alkalinity of the cleaning baths is checked at specified times and if necessary the solution is supplemented with new active ingredients or entirely renewed. This checking is performed either manually or locally using an automatic titrator. Here the alkalinity is generally checked by

10 titration with a strong acid. The operating personnel assess the alkalinity on the basis of the acid consumption and initiate the necessary measures, such as for example bath supplementation or bath renewal. This currently conventional method requires that operating personnel are

15 present in the vicinity of the cleaning bath at the required monitoring times. The shorter the desired monitoring interval, the greater the demands on the operating personnel for the monitoring measurements.

20 EP-A-806 244 has disclosed a method of automatically analyzing the pH-value of a solution and additionally dosing acid or lye automatically in the case of deviations. In this document the object is to maintain the pH-value of a liquid flow at a predetermined value. No acid-base

25 titration takes place in this method. Here it is necessary to monitor the functioning capability of the plant on site. It is not possible to intervene into the course of the pH-measurements and dosing measures from a remote location.

30 In the prior art it is known to analyze the non-ionic surfactants in aqueous process solutions, such as for example in cleaning baths, manually using a colour indicator. Conventionally one proceeds such that a reagent which forms a colour complex with non-ionic surfactants is

35 added to a sample taken from the process solution. Preferably this colour complex is extracted into an organic solvent not miscible in all proportions with water,

whereupon its light absorption at a specified wavelength is determined photometrically. Tetrabromophenolphthalein ethyl ester can be used for example as reagent for the formation of the colour complex. Prior to the extraction
5 into an organic solvent, preferably into a chlorinated hydrocarbon, a buffer system for the pH-range 7 is added to the process solution.

It is also known to analyze non-ionic surfactants in the
10 presence of ionic surfactants. Here the ionic surfactants are separated from the sample by an ion exchanger. The non-ionic surfactants not bound in the ion exchanger are analyzed with the aid of the refractive index of the solution exiting from the exchanger column. Preferably the
15 refractive index is measured as a function of the elution time, the integral for the part of the curve deviating from the refractive index of the pure eluent is determined, and this integral is compared with the values obtained from calibration measurements.

20 An alternative but less accurate approach consists in measuring the extreme value of the refractive index and determining the surfactants content therefrom by comparison with a calibration curve.

25 Anionic and cationic surfactants in aqueous solutions can be detected for example by titration using Hyamin^R1622 (= N-benzyl-N,N-dimethyl-N-4(1,1,3,3,-tetramethyl-butyl)-phenoxy-ethoxyethylammonium chloride) and potentiometric
30 end-point determination. For this purpose a known quantity of Na-dodecylsulfate is added to the sample, titration is performed using Hyamin, and the end-point of the titration is determined using an ion-sensitive electrode.

35 Alternatively, anionic surfactants can also be analyzed by titration with 1,3-didecyl-2-methylimidazolium chloride. An electrode with an ion-sensitive membrane is used as

detector. The electrode potential is a function of the concentration of the measuring ions in the solution.

Depending upon the result of this surfactant analysis,
5 which involves a large outlay in terms of personnel, the plant personnel supplement the process solution with one or more supplementary constituents. The method thus requires that operating personnel are present at the plant location at least at the surfactant analysis times. It is therefore
10 personnel-intensive, in particular in the case of multi-level operation. Documentation of the results for quality control and quality assurance necessitates an additional outlay.

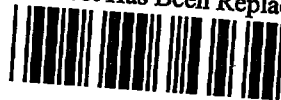
15 As a result of the cleaning process, the dirt constituents which have been removed from the surfaces accumulate in the cleaning solution. Pigment dirt can lead to loading with inorganic carbon. Corrosion protection oils, cooling lubricants or deformation agents, such as for example
20 drawing grease and/or organic coatings which have dissolved away or leached out, or jointing materials, lead to loading of the cleaning solution with total organic carbon. As the majority of this total organic carbon is present in the form of mineral oils, mineral fats, or oils and fats of
25 animal or vegetable origin, one often refers in abbreviated form to the "fat loading" of the cleaning solution. The majority of such oils and fats are present in emulsified form in the cleaning solution. Oils and fats of animal or vegetable origin can however be at least partially
30 hydrolysed by an alkaline cleaning solution. The hydrolysis products can then also occur in dissolved form in the cleaning solution. With too high a TOC loading of the cleaning solution it is no longer guaranteed that the cleaning solution will free the components to be cleaned of
35 oils and fats to the required extent. Or the danger exists that oils and fats will be drawn back onto the cleaned components when these are removed from the cleaning



solution. Therefore it is necessary to maintain the fat loading of the cleaning solution below a critical maximum value which can depend upon the further use of the cleaned components and upon the composition of the cleaning solution. In the case of a high fat loading, it is possible to increase the surfactants content of the cleaning solution in order to increase the fat-dissolving capacity of the cleaning solution. Or bath treatment measures are initiated with the aim of reducing the fat loading of the cleaning solution. This is in any case necessary at a predetermined upper limit of the fat loading. In the simplest case the cleaning solution is entirely or partially discarded and replaced or supplemented with fresh cleaning solution. However, on account of the waste water thereby produced and due to the need for fresh water, it is endeavoured to separate fats and oils from the cleaning solution and to continue to use the cleaning solution, optionally supplemented with active ingredients. Suitable devices for this purpose, such as for example separators or membrane filtration apparatus, are known in the art.

Previously it was customary to visually assess the cleaning efficiency of a cleaning solution on the basis of the cleaning result. The plant operating personnel assess the cleaning efficiency and implement the required measures, such as for example bath supplementation or bath renewal. This currently conventional method requires that operating personnel are present in the vicinity of the cleaning bath at the required monitoring times. The shorter the desired monitoring interval, the greater the demands on the operating personnel for the visual assessment.

In the prior art it has already been proposed that individual control parameters of cleaning baths be analyzed in program-controlled manner, the results of the analyses be transmitted to a remote destination and, depending upon



the result of the analyses, control measurements and/or bath treatment measures be initiated from the remote destination or also automatically and in program-controlled manner. A method of automatically monitoring and
5 controlling the surfactants content in aqueous process solutions is described in H 3267, the automatic analysis of the loading of aqueous cleaning solutions with carbon-containing compounds is described in H 3268, and the automatic monitoring and control of cleaning baths by
10 alkalinity analysis is described in German Patent Application DE 198 02 725.7. The present invention is based on these methods in that it links them with one another. The manner in which the individual analyses can be performed is described in detail in the three above
15 mentioned documents. The contents of these three documents are therefore also expressly to be considered as forming part of the present disclosure.

The object of the invention is to facilitate the
20 monitoring, and preferably also the control, of cleaning baths without the need for operating personnel to be present at the location of the cleaning bath.

Preferably the measuring device which is used is to be
25 self-checking and self-calibrating and in the event of a malfunction is to send an alarm signal to a remote location. Additionally, it is preferable to be able to check the functioning capability of the measuring device and the measurement results from a remote location.
30 Additionally, it is possible to intervene in the measurement process and the bath treatment measures from a remote location. By virtue of the desired remote monitoring, the personnel outlay for the bath monitoring and bath control of the cleaning baths is to be reduced.
35 Here it is to be provided that at least two parameters be analyzed, from which the functioning capability and/or dirt loading of the cleaning baths can be detected. By taking



into account several measured variables it is possible to initiate more purposive bath treatment measures than is possible when only one individual measured variable is known.

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This object is achieved by means of a method of monitoring cleaning baths, characterised in that at least two of the following analyses are performed in program-controlled manner:

- 10 i) analysis of the surfactants content,
 - ii) analysis of the loading with inorganic carbon and/or total organic carbon,
 - iii) analysis of the alkalinity
- and in that
- 15 a) depending upon the result of the analyses the additional dosing of supplementary constituents and/or one or more bath treatment measures is/are initiated and/or
 - b) the results of the analyses and/or data derived from
- 20 the results of the analysis are transmitted to at least one remote destination which is situated in a different room to the device for the implementation of the analysis.

25 For example, both the surfactants content and the loading with total organic carbon and/or inorganic carbon can be analyzed. Or the surfactants content and alkalinity are analyzed. Or the loading with total organic carbon and/or inorganic carbon and the alkalinity are analyzed.

30 Preferably however, all three parameters are analyzed in order to obtain a complete picture of the status of the cleaning bath.

The particular manner in which these analyses can be

35 performed in program-controlled fashion is described in detail in the above mentioned documents. The analyses can

be performed substantially simultaneously or also consecutively.

The result of the analysis can be stored on a data carrier.
5 Additionally or alternatively, it can form the basis of further calculations. The result of the analysis or the result of the further calculations is transmitted to a remote destination (= to a "remote location") where it is again stored on a data carrier and/or output. Where the
10 method according to the invention refers to a "remote destination" or a "remote location" this is to be understood as a location situated not in direct contact, or at least not in optical contact, with the process solution. The remote location can for example be a central process
15 control system which, as part of a total process for the surface treatment of the metal components, monitors and controls a cleaning bath as a subsidiary task. The "remote location" can also be an observation control centre from which the total process is monitored and controlled and
20 which is situated for example in a different room to the process bath. The "remote location" can also however be a location outside of the plant in which the cleaning bath is situated. In this way it is possible for specialists present outside the plant in which the process solution is
25 situated to check and control the process solution. As a result, the presence of specialist personnel at the location of the cleaning bath is far less often necessary.

Suitable data lines via which the analyses results and
30 control commands can be transmitted are available in the prior art. "Output of the result of the analysis or the further calculation" is to be understood in that the result is either forwarded to a superordinate process control system or is displayed on a screen and printed out so as to
35 be intelligible to a human. The location at which the result is displayed or output can correspond to the "remote location" defined in the foregoing. It is preferable for

the results of the individual analyses to be stored on a data carrier at least for a predetermined time interval to enable them to be subsequently evaluated, for example in the form of a quality assurance check. However the results of the analyses need not be directly output as such or stored on data carriers. Rather, they can also be used directly as the basis of further calculations, the results of these further calculations being displayed or stored. For example, in place of the instantaneous content, it is also possible to display the trend of the concentration and/or the relative change therein. Or the instantaneous contents are converted into "% of the nominal content" or "% of the maximum content".

Here the remote destination can be situated at a distance of at least 500 m from the device for the implementation of the analyses. In particular it can also be situated outside the plant in which the cleaning bath to be monitored is operated. Thus remote monitoring is provided without the need for operating personnel to be present in the direct vicinity of the cleaning bath.

Here it can be provided that the transmission of the results of the analyses and/or the data derived from the results of the analyses to the remote destination takes place automatically whenever new results of the analyses and/or data derived from the results of the analyses are determined. Alternatively, it can be provided that the transmission of the results of the analyses and/or the data derived from the results of the analyses to the remote destination takes place in response to a request from the remote destination.

The individual analyses can on the one hand be repeated after predetermined time intervals. Alternatively it can be provided in the program control that the individual analyses are repeated after time intervals which are the

shorter, the greater the difference between the results of two consecutive analyses. Here it can also be provided that the analysis of a second measured variable is initiated when the analysis of a first measured variable
5 has resulted in a predetermined critical value or a predetermined change in value between two analyses of this measured variable. The start of the analysis of one measured variable can thus be made dependent upon the result of the analysis of another measured variable.

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In other words: the method according to the invention can be performed in such a way that, in program-controlled manner, a second analysis selected from the analyses i), ii) and iii) is performed when a first analysis selected
15 from the analyses i), ii) and iii) supplies a result which overshoots a predetermined maximum value or undershoots a predetermined minimum value or deviates by a predetermined minimum value from the previous result of this first analysis.

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Naturally it can also be provided that the analyses are performed in response to a request from the remote destination.

25 In one embodiment, the method according to the invention is characterised in that, in program-controlled manner,

i) the analysis of the surfactants content is performed in that

- a) a sample of a predetermined volume is taken from
30 the aqueous process solution,
- b) if desired the sample is freed of solids,
- c) if desired the sample is diluted with water in a ratio which has been preset or is determined as a result of a preliminary analysis,
- 35 d) the surfactants content is analyzed by selective adsorption, electrochemically, chromatographically, by splitting into volatile

compounds, stripping-out and detecting these volatile compounds, or by the addition of a reagent which changes the interaction of the sample with electromagnetic radiation in proportion to the surfactants content, and measurement of the change in this interaction.

Another embodiment of the method according to the invention is characterised in that

- 10 ii) the analysis of the loading with inorganic carbon and/or total organic carbon is performed in that, in program-controlled manner,
 - a) a sample of a predetermined volume is taken from the aqueous cleaning solution,
 - 15 b) if desired the sample is freed of solids and/or homogenized,
 - c) if desired the sample is diluted with water in a ratio which has been preset or is determined as a result of a preliminary analysis,
 - 20 d) the content of inorganic carbon and/or total organic carbon in the sample is analyzed using known methods.

Depending upon the form of sub-step d), the content of inorganic carbon (IC), total organic carbon (TOC), or the sum thereof, total carbon (TC), can be analyzed. In particular, the proportion of lipophilic substances in the cleaning bath can be detected if, as part of the analysis, an extraction method is used in which only lipophilic substances are extracted from the cleaning solution and analyzed in a following step.

Another embodiment of the invention is characterised in that

- 35 iii) the alkalinity of the cleaning bath is analyzed by an acid-base reaction with an acid, wherein, in program-controlled manner,

- a) a sample of a predetermined volume is taken from a cleaning bath,
 - b) if desired the sample is freed of solids,
 - c) a selection is made whether free alkalinity
5 and/or total alkalinity is to be analyzed and
 - d) the sample is titrated by the addition of an acid or an acid is used as starting substance and titrated with the sample.
- 10 The sample volume taken in the respective sub-step a) can be permanently programmed into the control section of the measuring device to be used in the method. Preferably, the size of the sample volume can be changed from a remote location. Additionally, the control program can be
15 designed such that it makes the sample volume to be used dependent upon the result of a previous measurement. For example, the sample volume can be selected to be the greater, the smaller the content in the cleaning bath of the substance to be analyzed. The accuracy of the analysis
20 can thereby be optimised.

Between the taking of the sample and the actual measurement it can be desirable to free the sample of solids in the respective optional sub-step b). This is unnecessary in
25 the case of a cleaning solution with only a low solids loading. In the case of too high a solids content however, valves of the measuring device can become obstructed and sensors can become contaminated. Therefore it is advisable to remove solids from the sample. This can take place
30 automatically by filtration or also by the use of a cyclone or centrifuge.

Prior to the analysis of the selected parameter, if desired the sample is diluted with water in a ratio which is preset
35 or is determined as a result of a preliminary analysis. In sub-step d) the actual analysis is performed in accordance

with different methods which will be explained in detail later in the description.

In the simplest case the method according to the invention
5 operates such that the particular analyses are repeated after a predetermined time interval. The predetermined time interval will depend upon the requirements of the operator of the process solution and can comprise any desired time interval in the range from a few minutes up to
10 several days. For quality assurance it is preferable for the predetermined time intervals to range for example between 5 minutes and 2 hours. For example, a measurement can be performed every 15 minutes.

15 However, the method according to the invention can also be implemented in such manner that the particular analyses are repeated after time intervals which are the shorter, the greater the difference between the results of two consecutive analyses. The control system for the method
20 according to the invention can thus itself decide whether the time intervals between the individual analyses are to be reduced or increased. Naturally the instruction as to which time intervals are to be selected in the case of which differences between consecutive analyses must be
25 preset in the control system.

Here the two or three different analyses i), ii) and iii) need not always be performed consecutively in this sequence. Rather, it is possible for one analysis to be
30 performed more frequently than another. This will be the case if it is shown in practice that one parameter changes more rapidly than another. For example the surfactants content can be analyzed more frequently than the alkalinity. Or the plant is programmed such that the
35 decision whether another analysis is to be commenced is made dependent upon the result of the first analysis. For example it can be provided that an analysis of the

alkalinity is not performed until the carbon content of the cleaning bath overshoots a limit value to be predetermined. Or it is possible to analyze the alkalinity only when the surfactants content of the cleaning bath undershoots a lower limit to be determined. In this way it can for example be selected whether only the surfactants constituent or also the builder constituent need be added to the cleaning bath.

Furthermore, the method according to the invention can be implemented in such manner that the particular analyses are performed at any desired time in response to an external request. In this way, for example, immediate monitoring of the surfactants content, alkalinity and/or fat loading of the cleaning solution can be performed if quality problems are ascertained in subsequent process steps. The measurement of the selected analysis variable can thus take place in time controlled manner (at fixed time intervals) or in event-controlled manner (upon the ascertainment of changes or in response to external requests).

i) Analysis of the Surfactants Content

The method can be designed such that the surfactants whose content in the process solution is to be analyzed are non-ionic surfactants. For their analysis one can proceed such that in sub-step d) a reagent is added which changes the interaction of the sample with electromagnetic radiation in proportion to the content of non-ionic surfactants and the change in this interaction is measured.

For example, the reagent can consist of a complex of two substances A and B, where the non-ionic surfactants displace substance B from the complex it forms with substance A and the colour or fluorescence properties of substance B thereby change. For example, substance B can consist of a fluorescent substance or a dye capable of

forming a complex with for example dextrans or starch as an example of substance A. As a component of the complex, substance B has specific colour- or fluorescence properties. If it is displaced from the complex, these properties change. By measuring the light absorption or fluorescence radiation it is then possible to detect what proportion of substance B does not form a complex with A. Here substance A is selected such that upon the addition of non-ionic surfactants, substance B is displaced from the complex and instead a complex with the non-ionic surfactants is formed. Then the quantity of substance B displaced from the complex with A is proportional to the added quantity of non-ionic surfactants. From the change in the light absorption or fluorescence effected by the released quantity B, it is possible to deduce the quantity of added non-ionic surfactants.

For example, a salt of a cationic dye containing tetraphenylborate anions can be used as reagent. Non-ionic surfactants can displace the dye out of this salt when it has been converted into a cationic complex with barium by the addition of barium ions. This method of converting non-ionic surfactants into cationically charged complexes and thus making them accessible to reactions which respond to cations is also referred to in the art as "activation" of the non-ionic surfactants. The method is described for example by Vytras K., Dvorakova V, and Zeeman I (1989) in "Analyst" 114, p. 1435 ff. The quantity of cationic dye released from the reagent is proportional to the quantity of non-ionic surfactants present. If a change occurs in the absorption spectrum of the dye during this release, the released quantity of dye can be analyzed by photometric measurement of a suitable absorption band.

This analysis method can be simplified if a salt of a cationic dye soluble only in an organic solvent not miscible with water is used as reagent, while the released

dye itself is water-soluble and leads to a colouration of the water phase. Naturally the reverse is also suitable: a water-soluble salt of an organic dye is used, where the released dye is soluble only in an organic phase. By

5 releasing the dye in exchange for the non-ionic surfactants and extracting the released dye into the respective other phase, the dye can be photometrically analyzed therein in a simple manner.

10 This analysis method is also suitable for the analysis of cationic surfactants. As these are already inherently positively charged, the above described "activation" with barium cations is unnecessary.

15 Additionally, the reagent can consist of a substance which, with the anionic surfactants, itself forms a complex which has different colour- or fluorescence properties to the free reagent. For example, the reagent can be colourless in the optical domain while its complex with non-ionic
20 surfactants absorbs electromagnetic oscillations in the optical domain, and thus has a colour. Or the maximum of the light absorption, thus the colour, of the unbound reagent differs from that of the complex with the non-ionic surfactants. However, the reagent can also exhibit
25 specific fluorescence properties which change when it forms a complex with the non-ionic surfactants. For example, the free reagent can fluoresce, whereas the complex formation with the non-ionic surfactants extinguishes the fluorescence. In all cases, by measuring the light
30 absorption at a wavelength to be determined or by measuring the fluorescence radiation it is possible to analyze the concentration of the complex of reagent and non-ionic surfactants, and thus the concentration of the non-ionic surfactants themselves.

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Preferably in sub-step d) a reagent is added which, with the non-ionic surfactants, forms a complex which can be

extracted into an organic solvent not miscible in all proportions with water. Then the complex of non-ionic surfactants and added reagent is extracted into the organic solvent not miscible in all proportions with water. This
5 can be effected by intensive mixing of the two phases, for example by shaking or preferably by stirring. After this extraction step, the mixing of the two phases is terminated so that a phase separation into an aqueous and an organic phase occurs. If desired, the completeness of the phase
10 separation can be monitored by suitable methods, such as for example analysis of the electrical conductivity or measurement of the turbidity by light- absorption or scattering.

15 This is followed by the actual measurement of the content of non-ionic surfactants. For this purpose the organic phase containing the complex of non-ionic surfactants and added reagent is exposed to an electromagnetic radiation which can interact with the complex dissolved in the
20 organic phase. For example, visible or ultraviolet radiation can be used as electromagnetic radiation, the absorption of which by the complex of non-ionic surfactants and added reagent is analyzed. However it is also conceivable, for example, to use a reagent whose complex
25 with the non-ionic surfactants supplies a characteristic signal in the case of nuclear resonance- or electron spin resonance measurements. The signal strength, expressed as weakening of an electromagnetic oscillation in the appropriate frequency band (absorption), can be correlated
30 with the concentration of the complex. In place of absorption effects, emission effects can also be used to analyze the concentration. For example, a reagent can be selected whose complex with non-ionic surfactants in the organic solvent absorbs electromagnetic radiation of a
35 specific wavelength and in return emits electromagnetic radiation of a greater wavelength, the intensity of which is measured. An example in this respect is the measurement

of the fluorescence radiation when the sample is irradiated with visible or ultraviolet light.

In principle the mixing of the interaction of the organic phase with electromagnetic radiation can take place directly following the completion of the phase separation in the same vessel in which the phase separation is performed. However, depending upon the measurement method used to analyze the interaction of the organic phase with electromagnetic radiation, it is preferable for the organic phase, or a part thereof, to be drawn off and fed via a line to the actual measuring device. In this way, in particular it is possible to provide suitable cuvettes for the measurement. Accordingly, a preferred embodiment of the invention consists in that, in accordance with sub-step f), the organic phase is separated from the aqueous phase and fed to the measuring device. For this separation of the organic phase it is particularly advisable for the organic solvent not miscible in all proportions with water to consist of a halogen-containing solvent with a density greater than water. Following the implementation of the phase separation, the organic phase then is located in the lower part of the vessel and can be drawn off from the bottom.

For example dichloromethane or higher-boiling halogenated hydrocarbons, in particular chlorinated fluorocarbons, such as for example trifluorotrchloroethane are used as halogen-containing solvent. These solvents must be disposed of after use in accordance with the local legal regulations. As this can be costly, it is possible for the used solvent to be re-processed, for example by treatment with active carbon and/or by distillation, and re-used for the measurement process.

In a preferred embodiment of the invention a substance which in the organic phase forms a colour reaction with the

non-ionic surfactant is added as reagent. The light absorption at a predetermined wavelength can then be measured as the interaction of the organic phase with electromagnetic radiation. A conventional photometer is
5 suitable for this purpose. For example, tetrabromophenolphthalein ethyl ester can be used as colour reagent. In this case a buffer system with a pH-value in the region of 7 must be added to the sample of the aqueous process solution. Such a buffer system can consist for example of
10 an aqueous solution of dihydrogen phosphates and hydrogen phosphates. Here one preferably proceeds such that the quantity of the buffer solution substantially exceeds the sample quantity of the surfactant-containing process solution.

15 When tetrabromophenolphthalein ethyl ester is used as colour reagent, the measurement of the light absorption in sub-step g) preferably takes place at a wavelength of 610 nm.

20 In a preferred embodiment of the use of 3,3,5,5,- tetrabromophenolphthalein ethyl ester as colour reagent, the content of non-ionic surfactants can be analyzed as follows:

25 An indicator solution containing 100 mg 3,3,5,5,- tetrabromophenolphthalein ethyl ester in 100 ml ethanol is prepared. A buffer solution is also prepared by mixing 200 ml of a commercial buffer solution for the pH-value 7 (potassium dihydrogen phosphate/disodium hydrogen
30 phosphate) and 500 ml of a trimolecular potassium chloride solution with 1,000 ml water.

To perform the analysis, one commences with 18 ml of the buffer solution in a suitable vessel. To this is added
35 2 ml indicator solution. To this is added 50 μ l of the sample solution. The combined solutions are stirred for approximately 3 minutes and then 20 ml dichloromethane is

added. Then the vessel is vigorously mixed for approximately 1 minute. The phase separation is then awaited, which can for example take 20 minutes. Then the organic phase is removed and measured in a photometer at a wavelength of 610 nm. A 10-mm-cuvette is suitable for example as analysis cuvette. The surfactants content of the sample solution is determined with reference to a calibration curve.

10 If the surfactants content is so small that analysis becomes unreliable, the volume of the sample used for the measurement can be increased. If the surfactants content is so high that light absorption occurs above 0.9, it is advisable to dilute the sample prior to the measurement.

15 Irrespectively of the method selected, by means of a preceding calibration with surfactant solutions of known concentration, a correlation between the strength of the measurement signal and the concentration of the non-ionic surfactants must be established and stored. When the light absorption is measured, the calibration can also be effected by means of suitable coloured glass. As an alternative to preceding calibration, the surfactants content of the sample can be deduced by the addition of surfactant/reagent complex in a known concentration or by multiple build-up and re-measurement of the interaction with electromagnetic radiation.

As an alternative to analyzing the interaction with electromagnetic radiation of a reagent which binds to the non-ionic surfactant or is displaced from a complex therewith, it is also possible for the content of non-ionic surfactants to be analyzed chromatographically. For this purpose any oils and fats possibly present in the sample are firstly preferably removed. This can be effected for example by the use of an absorption agent. Then the sample, optionally containing ionic surfactants, is fed to

an anion- and/or cation exchanger column preferably in the form of a column for high-pressure/ liquid chromatography. The concentration of the non-ionic surfactants in the solution, freed of the ionic surfactants, issuing from the exchanger column is preferably analyzed via the refractive index. Here the quantitative evaluation is preferably performed in accordance with the external standard method. The measurement is performed by comparison with a pure solvent from the reference cell and solvent containing the substance to be analyzed from the measurement cell of the detector. Water or a water-methanol mixture is used as solvent.

Before the start of a series of measurements, the HPLC-like ion exchanger system must be calibrated and the reference cell of the detector must be flushed with the solvent for 20 minutes. Solutions in differing concentrations of the non-ionic surfactants to be analyzed are used for the calibration. Calibration- and sample solutions must be degassed in an ultrasonic bath for example for 5 minutes prior to injection into the HPLC-like system. The defined degassing is important due to the sensitivity of the refraction index detection to different solvent qualities.

If methanol is added to the sample solution prior to the transfer to the HPLC-like ion exchanger column, insoluble salts can precipitate. These must be filtered off by a micro-filter before the sample is fed to the HPLC-like system.

This method is known for the off-line analysis of unsulfonated constituents in organic sulfates or sulfonates (DIN EN 8799).

The following method is also suitable for the analysis of the non-ionic surfactants: The non-ionic surfactants are split with hydrogen halide, preferably with hydrogen

iodide, thus forming volatile alkyl halides, preferably alkyl iodides. By blowing a gas stream into the sample, the volatile alkyl halides are stripped out and detected in a suitable detector. An "electron capture detector" is
5 suitable for example for this purpose. This method is known as a laboratory method of characterising fatty alcohol ethoxylates (DGF Standard Method H-III 17 (1994)).

The surfactants can also be anionic surfactants. Their
10 content in the sample solution is analyzed in sub-step d), preferably electrochemically. For this purpose the anionic surfactants are titrated with suitable reagents, the titration being followed-up via the change in the electric potential of a suitable measuring electrode.

15 For example, here one can proceed in such manner that the pH-value of the sample is set in a range of between 3 and 4, preferably approximately 3.5, the sample is titrated with a titration reagent in the presence of an ion-
20 sensitive membrane electrode, and the change in the electrode potential is measured. The sensitivity of this method can be increased in that an alcohol containing 1 to 3 C-atoms, preferably containing methanol, is added to the sample. 1,3-didecyl-2-methylimidazolium chloride is
25 preferably suitable as titration reagent. An ion-sensitive membrane electrode, preferably with a PVC membrane, serves as measuring electrode. Such an electrode is known as "high sense electrode". A silver electrode is preferably used as reference electrode. The potential formation takes
30 place by means of as specific as possible an interaction between the ion carrier contained in the PVC membrane and the ions in the measured solution which are to be analyzed. This interaction, in the form of an equilibrium reaction, leads to a passage of the measured ions from the measured
35 solution into the membrane, and thus to the formation of an electric potential difference at the measured solution/membrane phase boundary. This potential

difference can be measured potentiometrically (currentlessly) using a reference electrode. The extent to which ions pass from the measured solution into the membrane is concentration-dependent. The relationship
5 between the measured ion concentration and the electric potential can be described theoretically by Nernst's equation. However, due to possible disturbances it is preferable to determine the relationship between electrode potential and measured ion concentration by calibration
10 with reference solutions.

Apart from anionic surfactants, cationic surfactants can also be analyzed in the process solution to be monitored. A method also suitable for the analysis of anionic
15 surfactants can be used for this purpose. Also in this method the analysis takes place electrochemically: a predetermined quantity of Na-dodecylsulfate is added to the sample, the sample is titrated using Hyamin (N-benzyl-N,N-dimethyl-N-4(1,1,3,3,-tetramethyl-butyl)-phenoxy-
20 ethoxyethylammonium chloride) and the titration end-point is determined using an electrode sensitive to ionic surfactants.

In addition to the methods described in the foregoing,
25 processes in which the surfactants are absorbed on suitable surfaces and in which effects due to the coating of the surfaces with the surfactants are measured, are suitable for analyzing the surfactants. As the coating of the surfaces with the surfactants below the saturation limit
30 can be considered as proportional to the surfactants content, after suitable calibration the surfactants content of the sample solution can be deduced from the changes in the properties of the surfactant-coated surfaces.

35 For example, the surfactants can be absorbed on the surface of an oscillator crystal and the change in the oscillating frequency of the oscillator crystal can be measured.

Another method consists of absorbing the surfactants on the - optionally suitably pretreated - surface of an optical conductor. This leads to a change in the refractive index upon the passage of light from the optical conductor into the surrounding medium, said change manifesting itself in the conductivity of the optical conductor to light. Depending upon the refractive index, the light in the optical conductor is weakened to a different extent or, in the event of a loss of total reflection, no longer appears at all at the end of the optical conductor. By comparing the light intensity emerging from the end of the optical conductor with that fed in at the start of the optical conductor, it is possible to determine the degree to which the surface of the optical conductor is coated with surfactants, and thus to determine the surfactants content in the surrounding medium. The collapse of the total reflection occurs at a specific threshold value of the surfactants content which can likewise be used to characterise the surfactants content of the process solution.

ii) Analysis of the Carbon Loading

The analysis of the loading with inorganic carbon and/or total organic carbon can be performed as described in detail in German Patent Application H 3268. Prior to the analysis of this parameter it is advisable to homogenise the sample, for example by vigorous stirring. This leads to a uniform and fine distribution of the organic impurities possibly present in the form of coarse oil or fat droplets.

If necessary, in sub-step c) the sample is diluted with water in a specified ratio. This ratio can be fixed but modifiable from a remote location. However, the dilution ratio can also be made dependent upon the result of a previous analysis of the content of inorganic carbon and/or total organic carbon. This ensures that the carbon content

of the sample solution is in a range which permits optimal analysis using the selected method.

In sub-step d) the inorganic carbon and/or total organic carbon can be analyzed for example by converting it into CO₂ and quantitatively determining the formed CO₂.

The conversion of the carbon into CO₂ by oxidation can be effected for example by combustion at an elevated temperature in the gas phase. The elevated temperature during the combustion is preferably greater than approximately 600°C, for example is approximately 680°C. Preferably the combustion is carried out using air or oxygen gas in a reaction pipe aided by a catalyst. Suitable catalysts are for example noble metal oxides or other metal oxides, such as for example vanadates, vanadium oxides, chromium-, manganese- or iron oxides. Platinum or palladium deposited on aluminium oxide can also be used as catalyst. This process directly provides a CO₂-containing combustion gas whose CO₂ content can be determined as described in the following.

As an alternative to combustion in the gas phase, the conversion of the carbon into CO₂ can also be effected by means of wet chemistry. Here the carbon of the sample is oxidized with a strong chemical oxidant, such as for example hydrogen peroxide or peroxodisulfate. If desired this wet-chemical oxidation reaction can be accelerated with the aid of a catalyst of the type referred to in the foregoing and/or with UV-radiation. In this case it is preferable to expel the formed CO₂ with a gas flow from the - if necessary acidified - sample for its quantitative determination. Carbon bonded in the form of carbonates or CO₂ can likewise be detected.

Irrespective of the method by which gaseous CO₂ has been generated, it can be quantitatively determined in

- accordance with one of the following methods. When the quantity of the sample is known, the content of inorganic carbon and/or total organic carbon in the cleaning solution can be calculated therefrom. Alternatively, using a
- 5 predetermined conversion factor, the result of the analysis is given in the form of fat loading per litre of cleaning bath if inorganic carbon is not present or has been previously removed.
- 10 Different methods known in the prior art can be used to analyze the CO_2 content of the obtained gas flow. For example, the gases can be passed through an absorber solution and for example the increase in weight of the absorber solution can be measured. An aqueous solution of
- 15 potassium hydroxide which absorbs CO_2 with the formation of potassium carbonate is suitable for example for this purpose. As an alternative to determining the increase in weight, it is possible to determine the change in the electric conductivity of the absorption solution or its
- 20 residual alkalinity following the absorption of the CO_2 .

The formed CO_2 can also be absorbed by a suitable solid whose increase in weight is measured. Soda asbestos is suitable for example for this purpose. Naturally it is

25 necessary to replace both an absorber solution and a solid absorber when they are exhausted and can no longer bind CO_2 .

However, for an automatically operating process it is simpler to quantitatively determine the CO_2 content of the

30 gas by measuring the infrared absorption. The determination of the infrared absorption can take place for example at a wavelength of $4.26 \mu\text{m}$ corresponding to a wave number of 2349 cm^{-1} . Devices capable of performing the combustion of the sample and the measurement of the

35 infrared absorption are known in the prior art. The TOC system of the company Shimadzu will be mentioned as an example.

For the photometric analysis of the CO₂ content of the combustion gas and the gas expelled from the sample it is possible to use not only dispersively operating infrared spectrometers but also non-dispersive photometers. These
5 are also known as "NDIR" devices. Such a device is described for example in DE-A-44 05 881.

In this analysis method the proportion of carbon deriving from deliberately added active ingredients in the cleaning
10 solution is also detected. Surfactants, organic corrosion inhibitors and organic complex-forming agents will be mentioned as examples. However, their content in the cleaning solution is known within specific fluctuation limits or can be separately defined. The proportion of
15 total organic carbon deriving from these active ingredients can thus be subtracted from the result of the analysis. The proportion deriving from the entered impurities is then obtained. In practice it is not essential here for the proportion of carbon present in the form of active
20 ingredients to be taken into account in the carbon analysis. Rather, it is often sufficient to fix an upper limit of the carbon content of the cleaning solution which itself takes into account the active ingredient content. By means of the carbon analysis it is then ascertained
25 whether the carbon loading is below or above this maximum limit.

The proportion of total organic carbon present in the form of lipophilic substances can alternatively be determined
30 such that the lipophilic substances are extracted into an organic solvent not miscible in all proportions with water. When the solvent has vaporized off, the lipophilic substances remain and can be gravimetrically analyzed. Preferably however, one proceeds such that the infrared
35 absorption of the lipophilic substances in the extract is photometrically analyzed. Halogenated hydrocarbons can be used in particular as organic solvent not miscible in all

proportions with water. A preferred example consists of 1,1,2-trichlorotrifluoroethane. This analysis method is based on DIN 38409, part 17, but in contrast to this method the proportion of lipophilic substances in the sample is
5 analyzed not gravimetrically following the evaporation of the organic solvent, but photometrically in the organic solvent. The quantitative analysis is preferably performed as in DIN 38409, part 18, by measuring the infrared
10 absorption of the lipophilic substances in the extract at a characteristic oscillation frequency of the CH_2 group. Here it is advisable for an organic solvent which itself contains no CH_2 groups to be used for the extraction. The infrared absorption band at $3.42 \mu\text{m}$ (2924 cm^{-1}) can be used for example for this photometric analysis. All the organic
15 substances which contain CH_2 groups and can be extracted into the organic solvent are now detected. In part these are also the surfactants in the cleaning solution. If this surfactant constituent is not to be detected it can be separately determined by an alternative method and
20 subtracted from the total result. If necessary, the distribution coefficient of the surfactants between the cleaning solution and the organic solvent not miscible in all proportions with water must be previously determined. In practice however it can be sufficient to fix a maximum
25 value of the permissible loading of the cleaning solution with lipophilic substances which additionally takes into account the surfactant constituent. If this maximum value is exceeded, bath treatment measures are to be initiated.

30 As part of this method it is advisable to calibrate infrared spectrometers with a known quantity of a lipophilic substance. A solution of 400 to 500 mg methylpalmitate in 100 ml 1,1,2,-trichlorotrifluoroethane can be used for example as calibrating solution. This
35 calibrating solution is likewise used to monitor the functioning of the IR-photometer.

Here one preferably proceeds by firstly adding a phosphoric acid magnesium sulfate solution to the sample of the cleaning solution. This solution is prepared by dissolving 220 g crystalline magnesium sulfate and 125 ml 85 wt.% phosphoric acid in deionised water and supplementing this solution with deionised water to 1000 g. The sample solution is mixed with approximately 20 ml of the phosphoric acid magnesium sulfate solution. Then 50 ml of the organic solvent not miscible in all proportions with water, preferably 1,1,2,-trichlorotrifluoroethane, is added. The aqueous and organic phases are mixed, a phase separation is performed, and the organic phase is isolated. Preferably this organic phase is again washed with the phosphoric acid magnesium sulfate solution, the phase separation is again performed, and the organic phase is drawn off. This is transferred into a measuring cuvette and the infrared absorption is measured at an oscillation band of the CH_2 -group. A suitable measuring cuvette consists for example of a quartz glass cuvette with a coating thickness of 1 mm. By comparison with the calibration curve, which also contains the blind value of the photometer, it is possible to determine the content of lipophilic substances in the sample on the basis of the infrared absorption.

In the implementation of the method according to the invention it can be desirable to detect both inorganic carbon and total organic carbon (TOC). This is the case for example when the sample is combusted for the analysis of the carbon content. Here dissolved CO_2 or carbon in the form of carbonates is additionally detected if CO_2 splits off from the carbonates at the selected combustion temperature. If in this case the inorganic carbon is not to be additionally measured, it can be removed in that the sample is acidified and the formed CO_2 is blown out with a gas such as for example air or nitrogen. This can be desirable if in a particular case only the "fat loading" of

the cleaning bath is to be determined. When the carbon content present in the form of lipophilic substances is analyzed in accordance with the above described extraction method, inorganic carbon automatically is not detected.

5

It is also possible for volatile organic compounds to be eliminated from the sample prior to the implementation of sub-step d) by expulsion with a gas, such as for example air or nitrogen. For example, volatile solvents can be eliminated in this way prior to the carbon analysis.

10

iii) Analysis of the Alkalinity

For the analysis of the alkalinity, one can proceed as described in German Patent Application DE 198 02 725.7.

15

In sub-step c), which is particular to this method, a selection is made whether the free alkalinity and/or the total alkalinity is to be analyzed. This can be permanently input into the program flow. For example, both the free alkalinity and the total alkalinity can be analyzed in an analysis cycle. However, the program can also decide to analyze one of these two values more often than the other. This can be the case for example when previous analyses have indicated that one of the two values changes more rapidly than the other. Naturally the choice as to whether free alkalinity or total alkalinity is to be analyzed can also be made by means of an external request. "External request" is to be understood in that intervention into the automated analysis process can be effected either by a superordinate process control system or manually via a data line.

20

25

30

The terms "free alkalinity" and "total alkalinity" are not clearly defined and are handled differently by the various users. For example, it is possible to define specific pH-values up to which titration must take place in order to analyze either the free alkalinity or the total alkalinity,

35

for example pH=8 for free alkalinity , pH=4.5 for total alkalinity. These preselected pH-values must be input into the control system for the automatic analysis process. As an alternative to specified pH-values, the transition
5 points of specific indicators can also be selected for defining the free alkalinity and the total alkalinity. Alternatively, inflection points in the pH-value curve can be selected and defined as equivalence points for the free alkalinity or the total alkalinity.

10

The acid-base reaction with an acid is used to actually analyze the alkalinity in sub-step d). Preferably a strong acid is chosen for this purpose. Here it is either possible to titrate the sample by adding an acid up to the
15 given criteria for free alkalinity or total alkalinity. Alternatively one can commence with the acid and titrate this with the sample.

Various sensors are suitable for following-up the acid-base
20 reaction of the cleaning solution with the acid used for the titration. In accordance with the current prior art, a pH-sensitive electrode, such as for example a glass electrode, will preferably be used. This supplies a pH-dependent voltage signal which can be further analyzed.
25 The use of such an electrode is particularly simple in terms of apparatus and therefore preferred.

However, the acid-base reaction of sub-step d) can also be followed-up using an indicator whose pH-dependent
30 interaction with electromagnetic radiation is measured. For example, this indicator can be a classical colour indicator whose colour change is photometrically measured. Alternatively, an optical sensor can be used. This consists for example of a film of an inorganic or organic
35 polymer containing a fixed dye which changes its colour at a specified pH-value. As in the case of a classical colour indicator, the colour change is based on the principle that

hydrogen ions or hydroxide ions which can diffuse into the film react with the dye molecules. The change in the optical properties of the film can be photometrically analyzed. As an alternative, it is possible to use films, 5 such as for example organic polymers, whose refractive index changes as a function of the pH-value. If for example an optical conductor is coated with such a polymer, total reflection can be obtained on one side of a threshold value for the refractive index in the optical conductor, so that 10 a light beam is propagated. However no total reflection occurs on the other side of the threshold value of the refractive index so that the light beam exits from the optical conductor. At the end of the optical conductor it can then be detected whether the light is propagated 15 through the optical conductor or not. Such a device is known as an "optrode".

Inorganic or organic solid bodies whose electrical properties change with the pH-value of the surrounding 20 solution can also be used as sensors. For example, an ion conductor whose conductivity is a function of the concentration of the H^+ - or OH^- -ions can be used. By measuring the d.c. or a.c. conductivity of the sensor, the pH-value of the surrounding medium can then be deduced.

25

Calibration/Control Measurements

Preferably the method according to the invention is performed such that the measuring device used for the individual analyses is self-monitoring and if necessary 30 self-calibrating. For this purpose it can be provided that the functioning capability of the measuring device used is checked after a predetermined time interval or after a predetermined number of analyses or in response to an external request, by control measurements of one or more 35 standard solutions. A standard solution with known values of the parameter to be analyzed is measured for checking purposes. This check is most realistic if a standard

cleaning solution whose composition is as close as possible to that of the cleaning solution to be checked is used as standard solution.

- 5 If, during a control measurement of a standard solution, the measuring device determines a value which differs from the nominal content by a minimum amount to be predetermined, the measuring device emits an alarm signal either locally or preferably at a remote location. Here
10 the alarm signal can contain an intervention proposal selected by the control program of the measuring device or by the superordinate process control system.

A key feature of the checking of the functioning capability
15 of the measuring device for the alkalinity consists in monitoring the sensor which is used. For example, this sensor can comprise a pH-sensitive electrode, in particular a glass electrode. Using a buffer solution as standard solution, it is possible to check whether the electrode is
20 supplying the expected voltage, whether it responds in the expected time interval, and whether its gradient (= voltage change as a function of the pH-change) lies in the desired range. If this is not the case, the measuring device emits an alarm signal either locally or preferably at a remote
25 location. Here the alarm signal can contain an intervention proposal selected by the control program of the measuring device or the superordinate process control system. For example it can be proposed that the electrode be cleaned or replaced.

30

In the method according to the invention it can also be provided that the functioning capability of the measuring device used is checked by a control measurement of one or more standard solutions if the results of two consecutive
35 measurements differ by a predetermined amount. In this way it is possible to distinguish whether established deviations in contents of the cleaning bath are real and

require bath treatment measures or whether they have been simulated by a fault in the measuring system.

Depending upon the result of the check on the measuring
5 device used, the analyses performed between the current and the previous control measurement can be provided with a status characteristic indicating the reliability of these analyses. If for example, consecutive control measurements for checking the measuring device used have shown that it
10 is operating correctly, the analyses can be provided with a status characteristic "OK". If the results of the control measurements differ by a predetermined minimum amount, the intervening analyses can be provided for example with the status characteristic "doubtful".

15 It can additionally be provided that, depending upon the result of the check on the measuring device used, the automatic analysis of the measured variables is continued and/or one or more of the following actions is performed:
20 analysis of established deviations, correction of the measuring device, termination of the analysis of the relevant measured variable, transmission of a status message or alarm signal to a superordinate process control system or monitoring device, thus to a remote location. If
25 desired, the measuring device can thus itself decide in accordance with preset criteria whether it is sufficiently capable of functioning so as to allow all the analyses to continue or whether deviations requiring manual intervention are ascertained.

30 Preferably, the measuring system employed in the method according to the invention is designed such that it automatically monitors the levels and/or consumption of the reagents and solvents used, as well as flushing solutions,
35 and upon the undershooting of a predetermined minimum level emits a warning signal. In this way it is possible to prevent the measuring device from becoming incapable of

functioning due to a lack of the required chemicals. The monitoring of the levels can take place in accordance with known methods. For example, the vessels containing the chemicals can be placed on scales which record the particular weight of the chemicals. Or a float is inserted. Alternatively, a minimum level can be checked by means of a conductivity electrode submerged in the vessel containing the chemical. The warning signal to be emitted by the measuring device is preferably transmitted to the remote location so that the appropriate measures can be initiated from there. In general, in the method according to the invention it is preferably provided that the results of the analyses and/or of the control measurements and/or of the calibrations and/or the status signals are transmitted to a remote location continuously or at predetermined time intervals and/or upon request. In this way, monitoring personnel, who are not required to be present at the location of the cleaning bath, are kept constantly informed about the bath's instantaneous alkalinity content. Depending upon the result of the analyses and control measurements, necessary corrective measures can be implemented either automatically via a process control system or by manual intervention.

As part of the method according to the invention it can be provided that for each analysis selected from the analyses i), ii) and iii), after a preset time interval or after a preset number of analyses or in response to a request from the remote destination, the functioning capability of the measuring device used is checked by a control measurement of one or more standard solutions and the result of the check is transmitted to the remote destination. Additionally, a corresponding check of the functioning capability of the measuring device used can be initiated when the results of two consecutive analyses differ by a predetermined amount. The result of this check is also preferably transmitted to the remote destination.

Depending upon the result of the check on the measuring device used, the analyses of the relevant measured variable performed between the current and preceding control measurement can be provided with a status characteristic
5 indicating the reliability of these analyses.

In the method according to the invention it can further be provided that, depending upon the result of one or more of the analyses selected from the analyses i), ii) and iii),
10 the additional dosing of supplementary constituents and/or one or more bath treatment measure(s) is/are initiated from the remote destination. Alternatively or additionally, it can be provided that, depending upon the result of one or more of the analyses selected from the analyses i), ii) and
15 iii), the additional dosing of supplementary constituents and/or one or more bath treatment measures is/are initiated in program-controlled manner.

Additionally, in the method according to the invention it
20 can be provided that the additional dosing of supplementary constituents and/or one or more bath treatment measures is/are initiated in program-controlled manner when predetermined relations between the results of at least two of the analyses selected from the analyses i), ii) and iii)
25 are ascertained. Thus specified relations between the results of the individual analyses i), ii) and iii) are preset in the control program for the process and when said relations come into effect supplementary constituents are additionally dosed and/or bath treatment measures are
30 initiated. The decision in this respect is thus made dependent not upon one single measured value but upon at least two measured values of different bath parameters. Here the relations in the case of which measures are initiated can be changed from the remote location, for
35 example in order to take into account operating experiences. For example it can be provided that a measure to reduce the fat loading of the cleaning bath be performed

(full or partial renewal of the bath, removal of fat and/or oil from the bath by separators and/or by membrane filtration methods) if on the one hand the content of total organic carbon overshoots a predetermined maximum content and on the other hand the surfactants content undershoots a predetermined minimum content. Or a specific maximum value is given for the sum of surfactants content and fat loading, above which a bath treatment measure is automatically initiated.

Depending upon the acquired measured value or the established change in the measured values, one or more of the following corrective measures can be initiated:

15 Correction and Bath Treatment Measures

The simplest corrective measure consists in that, upon the overshooting of a predetermined maximum value of inorganic carbon and/or total organic carbon or in response to an external request, a device is activated which doses one or more supplementary components (solution or powder) into the cleaning bath. This can take place for example in automated fashion in that, depending upon the determined carbon content, a specified quantity of supplementary solution or supplementary powder is supplied to the cleaning bath. Here it is possible to vary the size of the added portion itself or, in the case of fixed added portions, the time interval between the individual additions. This can be effected for example via dosing pumps or also in weight-controlled fashion. In the method according to the invention it is thus provided on the one hand that in the case of specific deviations from the nominal value (in particular when the functioning capability of the measuring device has been ascertained by the control measurements), a specified quantity of supplementary constituent is additionally dosed into the cleaning bath. Furthermore, it can be provided that these bath supplementing measures are performed when a

predetermined minimum change in the carbon content has been established. Furthermore however, this additional dosing can also take place in response to an external request, for example from a remote location, independently of the
5 instantaneous carbon content. The additional dosing, for example of surfactants, increases the carbon content of the cleaning solution. Upon the next analysis of the carbon content this must be taken into account in an appropriate manner, which can take place automatically. An addition of
10 surfactants increases the oil- and fat bearing capacity of the cleaning bath. Accordingly it is necessary to increase the tolerable maximum value of the carbon loading, the overshooting of which initiates the next bath treatment measure. This can be provided automatically in the control
15 program.

In place of an additional dosing of bath constituents, such as for example surfactants, or upon the overshooting of a predetermined maximum content of inorganic carbon and/or
20 total organic carbon, bath treatment measures can be initiated to reduce the content of inorganic carbon and/or total organic carbon in the cleaning solution. Such bath treatment measures have the aim in particular of reducing the fat- and oil content of the cleaning solution. In the
25 simplest example this can take place in that the cleaning solution is completely or partially discharged and replaced by fresh cleaning solution. It is more economical however to remove oils and fats from the cleaning solution by measures known in the prior art, such as separation by a
30 separator or separation by membrane filtration. As surfactants are also at least partially discharged in these processes, the cleaning solution must be supplemented appropriately. The initiation of these measures can also be made dependent not only upon the absolute carbon content
35 of the cleaning solution but also upon a predetermined change in the carbon content.

For the monitoring and control of the surfactants content and/or alkalinity, it can be provided that upon the undershooting of a predetermined minimum value of the content or in response to an external request, a device is
5 activated which doses one or more supplementary constituents into the cleaning solution. A supplementary solution containing all the active ingredients of the cleaning solution in the correct quantity ratio can be used for example as supplementary constituent. The
10 supplementary solution can thus contain not only the monitored contents but also further active ingredients of the cleaning solution, such as for example surfactants, builder substances, alkalis, complex-forming agents and corrosion inhibitors. Alternatively, the supplementary
15 solution can contain only surfactants or only alkalis while the other active ingredients of the cleaning solution are additionally dosed if necessary on the basis of separate analyses in clock-controlled or throughput-controlled manner.
20
Here it is possible to vary the size of the added portion itself or, in the case of fixed added portions, the time interval between the individual additions. This can be effected for example via dosing pumps or also in weight-
25 controlled manner. In the method according to the invention, thus on the one hand it is provided that in the case of specific deviations from the nominal value (in particular when the functioning capability of the measuring device has been ascertained by the control measurements) a
30 specified quantity of supplementary constituent is additionally dosed into the process solution. On the other hand however this additional dosing can also be performed in response to an external request, for example from a remote location, irrespective of the instantaneous content
35 of surfactants and/or alkalis.

In another embodiment of the invention, the process solution is supplemented in throughput-dependent manner with a predetermined quantity of supplementary constituent per throughput unit. For example, in the case of a
5 cleaning bath for automobile bodies it is possible to specify the quantity of supplementary constituent which is added in respect of each cleaned body. In accordance with the invention the monitoring of the surfactants content or alkalinity then serves to monitor and document the success
10 of this predetermined addition and, by additional result-dependent fine dosing and optionally also a discontinuation of the basic dosing, to achieve a more constant operating mode of the cleaning bath. Quality fluctuations are thereby reduced.

15 Naturally the method according to the invention requires that the appropriate device is available. This contains a control unit, for example a computer control unit, which controls the measurement process in time- and/or event-
20 dependent manner. It must also comprise the required reagent vessels, pipelines, valves, dosing- and measuring devices etc. for the control and measurement of the sample flows. The materials are to be adapted to the purpose of use, for example are to consist of high-grade steel and/or
25 plastics. The control electronics unit of the measuring device is to possess an appropriate input-output interface to permit communication with a remote location.

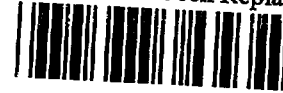
The method according to the invention on the one hand
30 enables contents of cleaning baths to be checked on site and predetermined corrective measures to be initiated without manual intervention. In this way the process reliability is improved and a constantly reliable cleaning result is obtained. Deviations from the nominal values can
35 be detected at an early point in time and corrected automatically or manually before the cleaning result is impaired. On the other hand, the measurement data are

preferably transmitted to a remote location so that operating- or supervisory personnel are kept constantly informed about the status of the cleaning bath even when they are not present in the direct vicinity of the bath.

- 5 The outlay in terms of personnel for monitoring and controlling the cleaning bath can thus be substantially reduced. The documentation of the data collected in the method according to the invention complies with the requirements of modern quality assurance. The consumption
10 of chemicals can be documented and optimised.

Claims

1. A method of monitoring cleaning baths, characterised
in that at least two of the following analyses are
5 performed in program-controlled manner:
i) analysis of the surfactants content,
ii) analysis of the loading with inorganic carbon
and/or total organic carbon,
iii) analysis of the alkalinity,
10 and that
a) depending upon the result of the analyses, the
additional dosing of supplementary constituents
and/or one or more bath treatment measures is/are
initiated and/or
15 b) the results of the analyses and/or data derived
from the results of the analyses are transmitted
to at least one remote destination which is
situated in a different room to the device for
the implementation of the analyses.
20
2. A method according to Claim 1, characterised in that
the remote destination is situated at a distance of at
least 500 m from the device for the implementation of
the analyses.
25
3. A method according to one or both of Claims 1 and 2,
characterised in that the transmission of the results
of the analyses and/or the data derived from the
results of the analyses to the remote destination
30 takes place automatically whenever new results of the
analyses and/or data derived from the results of the
analyses are determined.
4. A method according to one or both of Claims 1 and 2,
35 characterised in that the transmission of the results
of the analyses and/or the data derived from the
results of the analyses to the remote destination



takes place in response to a request from the remote destination.

5. A method according to one or more of Claims 1 to 4,
5 characterised in that the individual analyses are repeated after predetermined time intervals.
6. A method according to one or more of Claims 1 to 4,
10 characterised in that the individual analyses are repeated after time intervals which are the shorter, the greater the difference between the results of two consecutive analyses.
7. A method according to one or more of Claims 1 to 4,
15 characterised in that the analyses take place in response to a request from the remote destination.
8. A method according to one or more of Claims 1 to 4,
20 characterised in that, in program-controlled manner, a second analysis selected from the analyses i), ii) and iii) is performed when a first analysis selected from the analyses i), ii) and iii) supplies a result which overshoots a predetermined maximum value or undershoots a predetermined minimum value or differs
25 by a predetermined minimum value from the previous result of this first analysis.
9. A method according to one or more of Claims 1 to 8,
30 characterised in that, in program-controlled manner,
 - i) the analysis of the surfactants content is performed in that
 - a) a sample of a predetermined volume is taken from the aqueous process solution,
 - b) if desired the sample is freed of solids,
 - 35 c) if desired the sample is diluted with water in a ratio which has been preset or is determined as a result of a preliminary analysis,



- 5 d) the surfactants content is analyzed by selective adsorption, electrochemically, chromatographically, by splitting into volatile compounds, stripping-out and detecting these volatile compounds, or by the addition of a reagent which changes the interaction of the sample with electromagnetic radiation in proportion to the surfactants content, and measurement of the change in this interaction.
- 10 10. A method according to one or more of Claims 1 to 8, characterised in that
- ii) the analysis of the loading with inorganic carbon and/or total organic carbon is performed in that, in program-controlled manner,
- 15 a) a sample of a predetermined volume is taken from the aqueous cleaning solution,
- b) if desired the sample is freed of solids and/or homogenized,
- c) if desired the sample is diluted with water in a ratio which has been preset or is determined as a result of a preliminary analysis,
- 20 d) the content of inorganic carbon and/or total organic carbon in the sample is analyzed using known methods.
- 25 11. A method according to one or more of Claims 1 to 8, characterised in that
- iii) the alkalinity of the cleaning bath is analyzed by an acid-base reaction with an acid wherein, in program-controlled manner,
- 30 a) a sample of a predetermined volume is taken from a cleaning bath,
- b) if desired the sample is freed of solids,
- c) a selection is made whether free alkalinity and/or total alkalinity is to be analyzed and
- 35



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d) the sample is titrated by the addition of an acid or an acid is taken as starting substance and titrated with the sample.

- 5 12. A method according to one or more of Claims 1 to 11, characterised in that for each analysis selected from the analyses i), ii) and iii), after a predetermined time interval or after a predetermined number of analyses or in response to a request from the remote
10 destination, the functioning capability of the measuring device used is checked by a control measurement of one or more standard solutions and the result of the check is transmitted to the remote destination.
- 15 13. A method according to one or more of Claims 1 to 11, characterised in that for each analysis selected from the analyses i), ii) and iii), the functioning capability of the measuring device used is checked by
20 a control measurement of one or more standard solutions when the results of two consecutive analyses differ by a predetermined amount, and the result of the check is transmitted to the remote destination.
- 25 14. A method according to Claims 12 or 13, characterised in that, depending upon the result of the check on the measuring device used, the analyses performed between the current and the previous control measurement are provided with a status characteristic indicating the
30 reliability of these analyses.
15. A method according to one or more of Claims 1 to 14, characterised in that, depending upon the result of one or more of the analyses selected from the analyses
35 i), ii) and iii), the additional dosing of supplementary constituents and/or one or more bath



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treatment measures is/are initiated from the remote destination.

16. A method according to one or more of Claims 1 to 14,
5 characterised in that, depending upon the result of
one or more of the analyses selected from the analyses
i), ii) and iii), the additional dosing of
supplementary constituents and/or one or more bath
treatment measures is/are initiated in program-
10 controlled manner.
17. A method according to one or more of Claims 1 to 14,
characterised in that, in program-controlled manner,
the additional dosing of supplementary constituents
15 and/or one or more bath treatment measures is/are
initiated when predetermined relations between the
results of at least two of the analyses selected from
the analyses i), ii) and iii) are ascertained.