



Office de la Propriété
Intellectuelle
du Canada

Un organisme
d'Industrie Canada

Canadian
Intellectual Property
Office

An agency of
Industry Canada

CA 2079628 C 2001/12/11

(11)(21) **2 079 628**

(12) **BREVET CANADIEN
CANADIAN PATENT**

(13) **C**

(22) Date de dépôt/Filing Date: 1992/10/01

(41) Mise à la disp. pub./Open to Public Insp.: 1993/04/06

(45) Date de délivrance/Issue Date: 2001/12/11

(30) Priorité/Priority: 1991/10/05 (P 41 33 100.1) DE

(51) Cl.Int.⁵/Int.Cl.⁵ C23G 1/14

(72) Inventeurs/Inventors:
Blümlhuber, Georg, DE;
Wittel, Klaus, DE

(73) Propriétaire/Owner:
Metallgesellschaft Aktiengesellschaft, DE

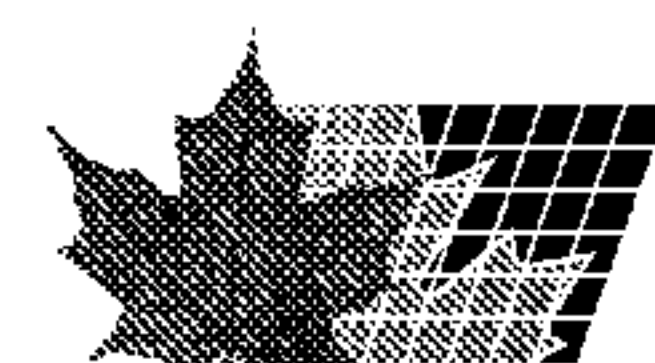
(74) Agent: ROBIC

(54) Titre : METHODE DE NETTOYAGE DE SURFACES METALLIQUES

(54) Title: PROCESS OF CLEANING METAL SURFACES

(57) **Abrégé/Abstract:**

In a process of cleaning metal surfaces with aqueous alkaline cleaning solutions, which contain silicates and surfactants and are recycled after ultrafiltration, a solution is employed which contains silicate only as a sodium silicate and/or potassium silicate of the general formula $\text{Na}_20.2\text{SiO}_2 \cdot x\text{H}_2\text{O}$ and/or $\text{K}_20.2\text{SiO}_2 \cdot x\text{H}_2\text{O}$. The cleaning solution is preferably adjusted to a pH value between 7 and 12 and to a concentration (expressed as SiO_2) of 0.1 to 20, particularly 0.5 to 10 g, silicate per liter.



ABSTRACT

In a process of cleaning metal surfaces with aqueous alkaline cleaning solutions, which contain silicates and surfactants and are recycled after ultrafiltration, a solution is employed which contains silicate only as a sodium silicate and/or potassium silicate of the general formula $\text{Na}_2\text{O} \cdot 2\text{SiO}_2 \cdot x\text{H}_2\text{O}$ and/or $\text{K}_2\text{O} \cdot 2\text{SiO}_2 \cdot x\text{H}_2\text{O}$.

The cleaning solution is preferably adjusted to a pH value between 7 and 12 and to a concentration (expressed as SiO_2) of 0.1 to 20, particularly 0.5 to 10 g, silicate per liter.

Metallgesellschaft AG

October 4, 1991

Reuterweg 14

6000 Frankfurt-on-Main 1

Case No. 91 00 35

Process of Cleaning Metal Surfaces

This invention relates to a process of cleaning metal surfaces with aqueous alkaline cleaning solutions, which contain silicates and surfactants and are recycled after ultrafiltration.

It is known to degrease and clean metal surfaces in that they are dipped into or sprayed with alkaline reacting products, which are composed of one or more alkaline reacting components, such as borax, sodium metasilicate, tertiary sodium phosphate, sodium pyrophosphate, sodium polyphosphate, sodium carbonate and sodium hydroxide, and the corresponding potassium compounds and in their commercially available forms have different water contents depending on the starting products. The content of the principal components and/or builder substances will particularly depend on the nature of the contamination, on the desired basicity and on the aggressive action on the material to be cleaned. Some of said cleaning agents have also small contents of organic surface active agents, such as ionic or nonionic surfactants and soaps (German Patent Publication 10 74 357). Known alkaline cleaning solutions

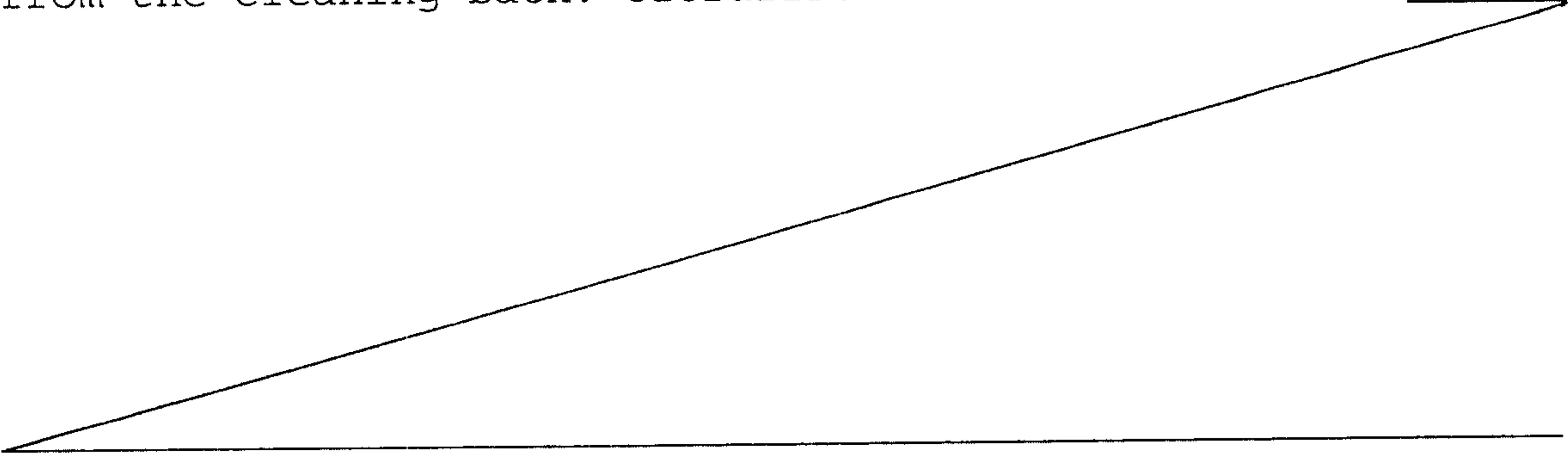
consist, e.g., of an aqueous solution of mixtures of sodium metasilicate, sodium carbonate, sodium hydroxide, and dodecyl benzene sulfonate or of sodium pyrophosphate, sodium polyphosphate, sodium tetraborate, sodium carbonate, and dodecyl benzene sulfonate (EP-A-0 372 610; DE 38 41 134).

From "Chem.-Ing.-Tech." 51 (1979), pages 662-664, it is also known in the metal-working industry to use ultrafiltration, e.g., to regenerate cleaning emulsions.

10 Aqueous cleaning solutions having pH values in the range of 4 to 13 and temperatures up to about 95°C are used to remove oil, grease, dirt and metal fines. The laden cleaning emulsions must be renewed from time to time. This involves a loss of valuable substances and a considerable burden by waste water. The regeneration of cleaning emulsions by ultrafiltration results in a considerable prolongation of the useful life of the cleaning solutions and in a considerable decrease of the amount of sewage.

The regeneration of the cleaning baths by ultra-

20 filtration technology is usually effected in that the high-oil retentate obtained by the ultrafiltration proper is fed to a recycling tank whereas the oil-free permeate is recycled to the cleaning bath. The recycling tank is fed from the cleaning bath. Ultrafiltration is effected



to an oil concentration of 10 to 40% in the retentate, which is subsequently disposed of, e.g., by incineration, optionally after a further concentrating treatment. Because most of the inorganic contents remain in the permeate and an oil increase by a factor of about 100 is achieved, that recycling prolongs the useful life of the cleaning solution correspondingly and relieves the sewage.

In the ultrafiltration the filtration rate will substantially depend on the difference between the pressures in front of and behind the membrane and on the temperature of the liquid to be filtered and in particular highly depends on the enriching of the retained components in front of the membrane.

If the widely used silicate-containing alkaline cleaning agents are used, the membrane will often be clogged. Such clogging will result in a rapid decrease of the flow rate expressed as the permeate volume per unit of time in the ultrafiltration. The reasons for that phenomenon have not definitely be clarified and said disadvantages have previously been tolerated.

It is an object of the invention to provide for the cleaning of metal surfaces with aqueous alkaline silicate-containing cleaning solutions and with simultaneous

use of ultrafiltration technology a process which is free of the disadvantages of known processes and has a distinctly higher tolerance to impurities formed in the process and, in particular, can be carried out for a longer time and more economically.

That object is accomplished in that the process of cleaning metal surfaces with aqueous, silicate- and surfactant-containing purging solutions, in which process the cleaning solution is recycled after ultrafiltration, is carried out in accordance with the invention in such a manner that the metal surfaces are cleaned with a solution which contains silicate only as sodium silicate and/or potassium silicate of the general formula $\text{Na}_2\text{O} \cdot 2\text{SiO}_2 \cdot x\text{H}_2\text{O}$ or $\text{K}_2\text{O} \cdot 2\text{SiO}_2 \cdot x\text{H}_2\text{O}$.

It has surprisingly been found that the ultrafiltration membrane will be clogged only after a prolonged use and that permeate will flow for a much longer time until the flow rates become intolerably low.

The sodium silicate and potassium silicate used in the process in accordance with the invention may also be defined by the general formula $(\text{Na}_2\text{Si}_2\text{O}_5)_x \cdot y\text{H}_2\text{O}$ or $(\text{K}_2\text{Si}_2\text{O}_5)_x \cdot y\text{H}_2\text{O}$ and are commercially available as so-called disilicates. Owing to their chemical constitution they are special silicates of a leaf-like or layer-like structure. Regarding their microstructure and their properties they

differ substantially from the silicates which contain the anion $(\text{Si}_2\text{O}_7)^{6-}$ as a moiety and which are not used in the cleaning solutions for the process in accordance with the invention.

The silicate is preferably used in the form of a sodium salt. The sodium silicate is known and commercially available as a hydrous amorphous product or an anhydrous crystalline product and can be employed in both forms in the cleaning solution used in the process in accordance
10 with the invention. Such alkali silicates, such as the commercially available sodium disilicate, have a SiO_2 to Na_2O molar ratio of 2.06 to 2.14. Amorphous hydrous products have approximately the composition 27.5% Na_2O , 57.0% SiO_2 , 15.5% H_2O .

Commercially available substances are, e.g., the amorphous hydrous product "CupanonDI*" of van Baerle in Gernsheim, Germany, or the crystalline "Schichtsilikat* SKS-6" of Hoechst AG, Frankfurt, Germany.

According to a preferred feature of the inven-
20 tion the process is carried out with a cleaning solution having a pH value < 12.0 so that the cleaning solution does not contain free sodium hydroxide or potassium hydroxide.

According to a further feature of the process in accordance with the invention the concentration of alkali silicate (expressed as SiO_2) in the cleaning solution employed is 0.1 to 20 g/l and more preferably 0.5 to 10 g/l.

* trademarks

In order to avoid disadvantages in the preparation of the cleaning solution and in the addition of water to compensate losses caused by evaporation and entraining, it is desirable to use softened water and particularly deionized water.

The cleaning solution is preferably used in a dipping process although other application technologies, such as spraying, flooding and the like, may also be used.

The cleaning solution is normally used at elevated temperatures in excess of 50°C and up to its boiling point. Temperatures from about 55 to about 70°C are suitably employed.

The process in accordance with the invention will be explained more in detail and by way of example in the following examples.

In the examples, various cleaning solutions were employed to clean oil-soiled deep-drawn parts of sheet steel (RSt 1405). The flow rate of permeate was compared with that of water at 60°C. The membrane was regarded as being clogged when the flow rate had decreased to 20% of the value for water. The experiments were carried out with a laboratory system of Eisenmann, Holzgerlingen, Germany, and with an inorganic membrane of the type Carbosep^(R) having a separating size of 160.00 daltons measured with dextran. The surfactant used in all examples

consisted of a mixture of equal parts of dodecyl benzene sulfonate (Lutensit^(R) ALBN of BASF AG) and nonyl phenol polyethylene glycol ether (Arkopal^(R) N 100 of Hoechst AG).

Example 1 (control example)

To prepare to the cleaning solution, 20 g sodium metasilicate ($\text{Na}_2\text{SiO}_3 \cdot 5\text{H}_2\text{O}$) per liter of solution, corresponding to about 10 g/l SiO_2 , were dissolved in water having a hardness corresponding to 100 mg CaO per liter, and 2 g/l surfactant were added. The pH value of the solution was about 13. The solution was recycled after ultrafiltration. After about 2 hours the flow rate of permeate had decreased to 20% of the initial value for water.

Example 2 (in accordance with the invention)

Anhydrous crystalline sodium disilicate $\text{Na}_2\text{Si}_2\text{O}_5$ (Schichtsilikat SKS-6 of Hoechst AG) was dissolved in deionized water to prepare a solution of 20 g disilicate per liter of solution, corresponding to about 13 g/l SiO_2 , and 2 g/l surfactant were added. The pH value of the solution was about 11.5. The solution was recycled after ultrafiltration. After a filtration for 46 hours the flow rate of permeate had decreased only to about 40% of the initial value.

Example 3 (control example)

A solid cleaning agent concentrate composed of 20% $\text{Na}_2\text{SiO}_3 \cdot 5\text{H}_2\text{O}$, 25% $\text{Na}_4\text{P}_2\text{O}_7$, 25% $\text{Na}_5\text{P}_3\text{O}_{10}$, 15% NaHCO_3 ,

10% Na_2CO_3 , 5% surfactant was dissolved in deionized water to prepare a solution containing 30 g concentrate per liter of solution. The pH value of the solution was 11.6. The solution was recycled after ultrafiltration. After 1.5 hours the permeate flow rate had decreased to 20% of the initial value.

Example 4 (in accordance with the invention)

A solid cleaning agent concentrate composed of 17.3% $\text{Na}_2\text{Si}_2\text{O}_5$ (Cupanon DI of van Bearle), 7.0% NaOH , 15.0% NaHCO_3 , 10.0% Na_2CO_3 , 23.0% $\text{Na}_4\text{P}_2\text{O}_7$, 22.7% $\text{Na}_5\text{P}_3\text{O}_{10}$, 5.0% surfactant, was dissolved in softened water to prepare a solution containing 30 g concentrate per liter of solution. The pH value of the solution was 11.6. The solution was recycled after ultrafiltration. After about 16.7 h the flow rate of permeate had decreased to 50% of the initial value.

From the examples of the process in accordance with the invention it is apparent that in the cleaning metallic solutions with a cleaning solution which is ultrafiltered the useful life of the cleaning solution will considerably be increased if a cleaning solution is employed which contains silicate only as disilicate of the general formula $\text{Na}_2\text{O} \cdot 2\text{SiO}_2 \cdot x\text{H}_2\text{O}$ and/or $\text{K}_2\text{O} \cdot 2\text{SiO}_2 \cdot x\text{H}_2\text{O}$.

WHAT IS CLAIMED IS:

1. A process for cleaning metal surfaces with aqueous alkaline cleaning solutions, which contain silicates and surfactants and are recycled after ultrafiltration, wherein the metal surfaces are cleaned with a solution which contains silicate only as sodium silicate and/or potassium silicate of the general formula $\text{Na}_2\text{O} \cdot 2\text{SiO}_2 \cdot x\text{H}_2\text{O}$ or $\text{K}_2\text{O} \cdot 2\text{SiO}_2 \cdot x\text{H}_2\text{O}$.
2. A process according to claim 1, wherein the
10 metal surfaces are cleaned with a solution that is adjusted to a pH value between 7 and 12.
3. A process according to claim 1 or 2, wherein the metal surfaces are cleaned with a solution which contains silicate in a concentration, expressed as SiO_2 , of 0.1 to 20 g of silicate per liter.
4. A process according to claim 3, wherein said concentration of silicate in the solution is of 0.5 to 10 g of silicate per liter.
5. A process according to claim 1 or 2, wherein
20 the metal surfaces are cleaned with a solution which has been prepared with softened water.
6. A process according to claim 1 or 2, wherein the metal surfaces are cleaned with a solution which has been prepared with deionized water.

7. A process according to any one of claims 1 to 6, wherein said solution is regenerated by subjecting it to an ultrafiltration through an ultrafiltration membrane.

8. A process according to claim 7, wherein the permeate solution of said ultrafiltration is used for treating metal surfaces, with said permeate solution at a temperature and for a time sufficient to clean said metal surfaces.