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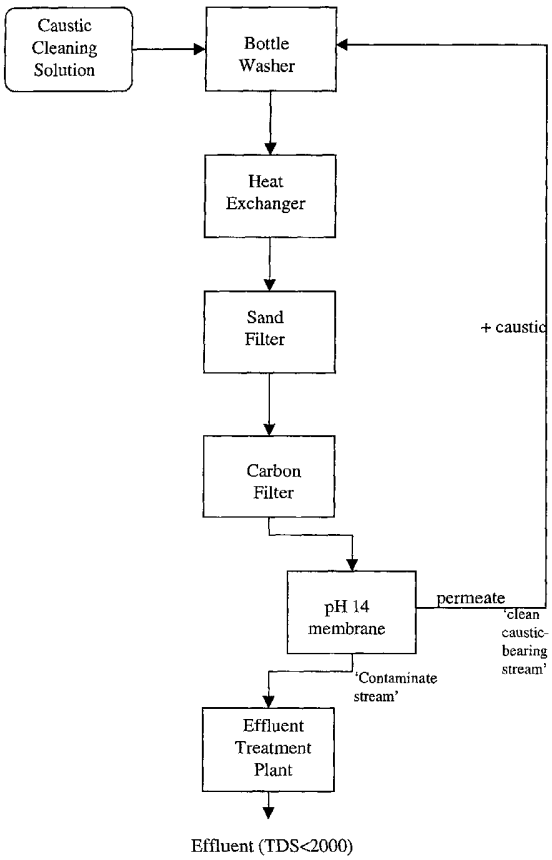
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[Continued on next page]

(54) Title: IMPROVEMENTS RELATING TO WATER TREATMENT



(57) Abstract: A process for the treatment of a contaminated caustic effluent stream is described. It comprises the steps of: a. passing the stream through a strong alkali resistant membrane; and b. producing a separate clean caustic-bearing stream and a separate residual contaminate stream; without neutralising the contaminated caustic streamprior to passing the stream through the membrane. By using a strong alkali resistant membrane, the caustic constituents of the contaminate effluent stream do not need to be neutralised with acid, often hydrochloric acid, thereby forming large concentrations of sodium chloride, i.e. salt. By reducing the salinity in the effluent this reduces the environmental impact of the overall effluent, and also makes it possible to recover and reuse the contaminate stream for irrigation or secondary water services. The process is particularly applicable to washing and cleaning glass bottles.

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For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

Improvements Relating to Water Treatment

The present invention relates to improvements relating to water treatment, in particular the recovery of alkalis/salts in aqueous solution using a membrane technique.

Highly alkaline solutions of chemicals in water, principally sodium hydroxide, soaps and detergents, are used for the cleaning of various components such as bottles for beverages and milk, metal parts, etc.

In the beverage industry, particularly in Africa and Asia, the use of returnable glass bottles (RGBs) requires substantial natural and synthetic resources in the form of water, chemicals and energy to be utilised to recover the RGBs into a clean and sterile state for re-use. The automated machinery for bottle washing uses large quantities of water heated to 60-70^{0}C, and containing sodium hydroxide (typically 2-3%) as the primary cleansing fluid with a fresh water rinse at the end of the cycle. Each plant typically produces around 20m^3/h of effluent

from the bottle washer during its operational run, the cleaning being a cascade of 2-3 passes of the cleaner with a bleed to effluent as fresh water is introduced for the final rinse.

In many of the countries which undertake this operation the contaminants generated as a by-product of bottle washing form a major impact on the water resources available. This impact is due to contaminating the wastewater produced with saline products and thus making the recycling of effluent difficult to achieve efficiently, as the by-product water generated from such a recycle operation is injurious to the environment.

The preservation of local water resources, reduced energy demand and environmental burden along the supply chain life cycle (i.e. the manufacture and supply of caustic) and reduction in risk to human safety and health (transporting and transferring bulk caustic) are powerful environmental drivers for the implementation of the technology.

The present practice is to remove the alkali from the effluent by neutralisation with acid. The neutralisation reaction can be by direct acid addition and/or by using a cation column which will subsequently be regenerated by hydrochloric or sulphuric acid. The former acid is predominantly used and causes the residual 0.05-0.15% caustic to become a saline effluent, carrying 0.08-0.24% sodium

chloride. It is desired to reduce this saline component in the effluent.

Thus, according to one aspect of the present invention, there is provided a process for the treatment of a contaminated caustic effluent stream comprising the steps of:

(a) passing the stream through a strong alkali resistant membrane; and

(b) producing a separate clean caustic-bearing stream and a separate residual contaminate stream;

without neutralising the contaminated caustic stream prior to passing the stream through the membrane.

By using a strong alkali resistant membrane, the caustic constituents of the contaminate effluent stream do not need to be neutralised with acid, often hydrochloric acid, thereby forming large concentrations of sodium chloride, i.e. salt. By reducing the salinity in the effluent this reduces the environmental impact of the overall effluent, and also makes it possible to recover and reuse the contaminate stream (after further cleaning) for irrigation or secondary water services, (because of the reduction in the salt content).

The term "contaminated caustic effluent stream" is well known in the art, and generally relates to an

effluent stream from a cleaning process involving a percentage, generally 2-3% but possibly lower or higher than this amount, of one or more caustic cleaning compounds.

The term "caustic" as used herein refers to compounds which can act as a strong alkali, and is not limited to sodium hydroxide. Compounds which can act as strong alkalis generally have a pH in the range 12-14, and are well known in the art.

The term "strong alkali resistant membrane" relates to any membrane capable of acting at the pH of a strong alkali, generally above pH11, and usually in the range pH12 or above, up to pH14.

Generally, the membrane is a nanofiltration membrane. Preferably, the membrane is adapted to allow passage of the caustic-bearing solution, whilst retaining in the reject stream heavy metal ions which are typically divalent and trivalent species. In the washing of returnable glass bottles, such heavy metal ions typically come from crown closures and labels and debris.

Some of the residual caustic may pass through the membrane into the contaminate stream which is dependant on the competing ions at the membrane interface. They can be neutralised at that time in a known manner such as with acid solution or on a cation column. However, typically the amount of caustic in the contaminate stream will not be so

significant that acid addition increases the salinity to significantly effect recovery of the contaminate stream for subsequent use in e.g. irrigation or secondary water services.

Strong alkali resistant membranes are known in the art, such as that in European Patent Application No 1044718A of Nikko Denko Corporation. Membranes formed by the invention of EP-A-1044718 have been found to be resistant to pH14 liquors, and have a porosity rating which allows for the passage e.g. of sodium hydroxide whilst rejecting heavy metal contaminants.

The process of the present invention may be carried out at elevated temperatures, e.g. 35°C, to promote univalent salt passage through the membrane.

Testing has found that the use of a strong alkali resistant nanofiltration membrane provides recovery of approximately 80-85% of the caustic in the caustic-bearing stream, leaving only residual approximately 15-20% in the contaminate stream.

As mentioned above, such trace caustic in the contaminate stream can be e.g. absorbed on a de-causticiser cation unit.

Preferably, the clean caustic-bearing stream is reusable, more preferably re-usable with the cleaning process from which the contaminated caustic

effluent stream originated. That is, a looped system.

Generally, reuse of the clean caustic-bearing stream requires re-dosing of the stream with a, generally, the relevant, caustic compound to increase the caustic concentration back to a desired level, e.g. 2-3%, for cleaning.

Alternatively, the clean caustic-bearing stream is concentrated, for example by a factor of 10, prior to re-use.

The present invention is useable with any contaminated caustic effluent stream. Such streams can be used in the cleaning or other processes involving caustic systems, including but not limited to one or more of recycling, washing, cleaning, etc of bottles, metals, etc.

The present invention will generally be part of a larger cleaning treatment process, which involves other filtration steps, such as carbon filtration, and the like, all known in the art.

It has been found particularly useful in the recovery and regeneration of water used in the cleaning of glass bottles. Typically, the effluent from the bottle washer is passed through a heat exchanger, sand filter, carbon filter, cation column with acid addition, leading to a final effluent treatment plant (see Figure 1). This is typically

provided an effluent from a treatment plant of a stream having a Total Dissolved Salts ("TDS") content of over 2000ppm, which is now becoming the general environmental upper level of TDS water content that allows the water to be reused.

The present invention avoids the need for the acid addition, and the resultant significantly high salinity in the effluent stream.

Thus, according to one preferred embodiment of the present invention, there is provided a process for treating the effluent of a bottle washer comprising the steps of;

(a) passing the bottle washer effluent through one or more of a heat exchangers and/or coarse filters;

(b) passing the effluent of step (a) through a strong alkali resistant membrane to provide a separate clean caustic-bearing stream and a separate residual contaminate stream;

(c) recycling the caustic-bearing stream, optionally with the addition of further caustic therewith; and

(d) treating the contaminate stream of step (b) to provide a final stream having a TDS content of less than 2000.

According to a second aspect of the present invention, there is provided a water treatment plant having a strong alkali resistant membrane unit through which contaminated caustic effluent stream can be passed, and which plant does not include means to neutralise the caustic stream prior to passage through the membrane.

According to a third aspect of the present invention, there is provided the use of a strong alkali resistant membrane in the treatment of contaminated caustic effluent stream.

An embodiment of the present invention will now be described by way of example only and with reference to the accompanying flow charts in which;

Figure 1 is a prior art bottle washer effluent stream treatment process; and

Figure 2 is a bottle washer effluent stream treatment process according to the present invention.

Referring to Figure 1, there is shown the general process steps used to treat the effluent of a returnable glass bottles (RGB) plant. The automated machinery for bottle washing uses large quantities of water heated to 60-70°C containing sodium hydroxide, typically of a concentration of 2-3%, as the primary cleansing fluid, with a fresh water rinse at the end of each cycle. The sand filter

provides protection of the membrane from gross suspended solids contamination, and the carbon filter provides biological and colour removal treatment.

The caustic is then neutralised by direct acid addition and/or by using a cation column. This generally creates very high levels of sodium chloride, rendering the treated effluent water as unusable. The ability of the effluent stream to add value is based on the physical and chemical characteristics which enable the treated effluent to be utilised and so save new water resources being consumed. The level of salinity may not allow water to be recovered by reverse osmosis as the concentrate so derived would become injurious to the environment or to subsequent processing plant. In an extreme case the effluent as treated may so compromise discharge that it may require a carrier water stream to allow its disposal. In this instance the effluent not only presents severe environmental impact but also increases the water consumed to affect its discharge.

An embodiment of the present invention is shown in Figure 2. The initial treatment steps are the same as in Figure 1, but after the carbon filter, a pH14 membrane cast from polysulfone and characterised as a nanofiltration membrane with a nominal cut off in the range 100 - 200K Daltons is used to provide a 'clean caustic-bearing stream' as a permeate, and a contaminate stream. Prior to the nanofiltration

there could be an optional ultrafiltration step to reduce suspended solids and fouling of the nanofiltration membrane.

Typically, the effect of the process is to reduce by at least 50%, generally greater, the saline content of the contaminate stream. Typically, the caustic bearing stream will have a caustic content of 0.05-0.1% sodium hydroxide. The recovered 'clean' caustic water stream is suitable for reuse, with the caustic quantity typically being approximately 70-80% of the feed load in 80-85% of the feed volume. Dosing of this stream with further sodium hydroxide allows it to be recycled or reused in the bottle washer, where a sodium hydroxide concentration is typically 3%.

The final effluent treatment plant generally involves the use of a reverse osmosis (RO) membrane. Such a membrane can concentrate the salt content in the contaminate stream by 3-4 times, and the reduction is saline content of the incoming stream will therefore allow the effluent to be reduced by 30% of its volume, and still meet discharge limits which are supposed to protect the environment, (generally TDS <2000).

In general, the recovered 70% of the water can still be reused, and, similar to the caustic water recovery, reduce the input of fresh water. Fresh water is a scarce commodity in some countries, and the process of the present invention reduces the cost of water produced, and treated for the RGB

facility, whilst decreasing the environmental impact of the manufacture and bottle washer.

This not only improves the environmental impact of the overall factory effluent but results in a reduction of pollution and the conservation of energy, minerals resources in the water. It also means a reduction in the unit cost of washing returnable glass bottles.

Claims

1. A process for the treatment of a contaminated caustic effluent stream comprising the steps of:

   a. passing the stream through a strong alkali resistant membrane; and

   b. producing a separate clean caustic-bearing stream and a separate residual contaminate stream;

without neutralising the contaminated caustic stream prior to passing the stream through the membrane.

2. A process as claimed in Claim 1 wherein the membrane is a nanofiltration membrane.

3. A process as claimed in Claim 1 or Claim 2 wherein the membrane is adapted to allow passage of the caustic-bearing solution, whilst retaining in the residual stream heavy metal ions.

4. A process as claimed in any one of the preceding claims wherein any residual caustic passing through the membrane into the contaminate stream is neutralised.

5. A process as claimed in Claim 4 wherein residual caustic is neutralised by absorption on a de-causticiser cation unit.

6. A process as claimed in any one of Claims 1 to 5 wherein the membrane is a pH14 membrane cast from polysulfone, with a nominal cut off in the range 100-200K Daltons.

7. A process as claimed in any one of the preceding claims wherein the process is carried out at an elevated temperature to promote univalent salt passage through the membrane.

8. A process as claimed in any one of the preceding claims wherein the clean caustic-bearing stream is reusable.

9. A process as claimed in Claim 9 wherein the clean caustic-bearing stream is reusable in the process from which the caustic effluent stream originated.

10. A process as claimed in any one of the preceding claims wherein the treatment is for cleaning a caustic stream.

11. The process as claimed in Claim 10 wherein the caustic stream originates from a process for recycling, washing and/or cleaning of bottles and/or metals.

12. A process as claimed in any one of the preceding claims wherein the process is used in the recovery and regeneration of water used in the cleaning of glass bottles.

13. A process for washing and cleaning glass bottles wherein the effluent from the bottle washer is passed through a heat exchanger, sand filter, carbon filter, cation column with acid addition, followed by a process as claimed in any one of Claims 1 to 9.

14. A process as claimed in any one of the preceding claims for treating the effluent of a bottle washer comprising the steps of;

a. passing the bottle washer effluent through one or more of a heat exchangers and/or coarse filters;
b. passing the effluent of step (a) through a strong alkali resistant membrane to provide a separate clean caustic-bearing stream and a separate residual contaminate stream;
c. recycling the caustic-bearing stream; and
d. treating the contaminate stream of step (b) to provide a final stream having a TDS content of less than 2000.

15. A water treatment plant having a strong alkali resistant membrane unit through which contaminated caustic effluent stream can be passed, which plant does not include means to neutralise the caustic stream prior to passage through the membrane.

16. A water treatment plant as claimed in Claim 16 involving a process as claimed in any one of Claims 1 to 14.

17. Use of a strong alkali resistant membrane in the treatment of contaminated caustic effluent stream.

Figure 1

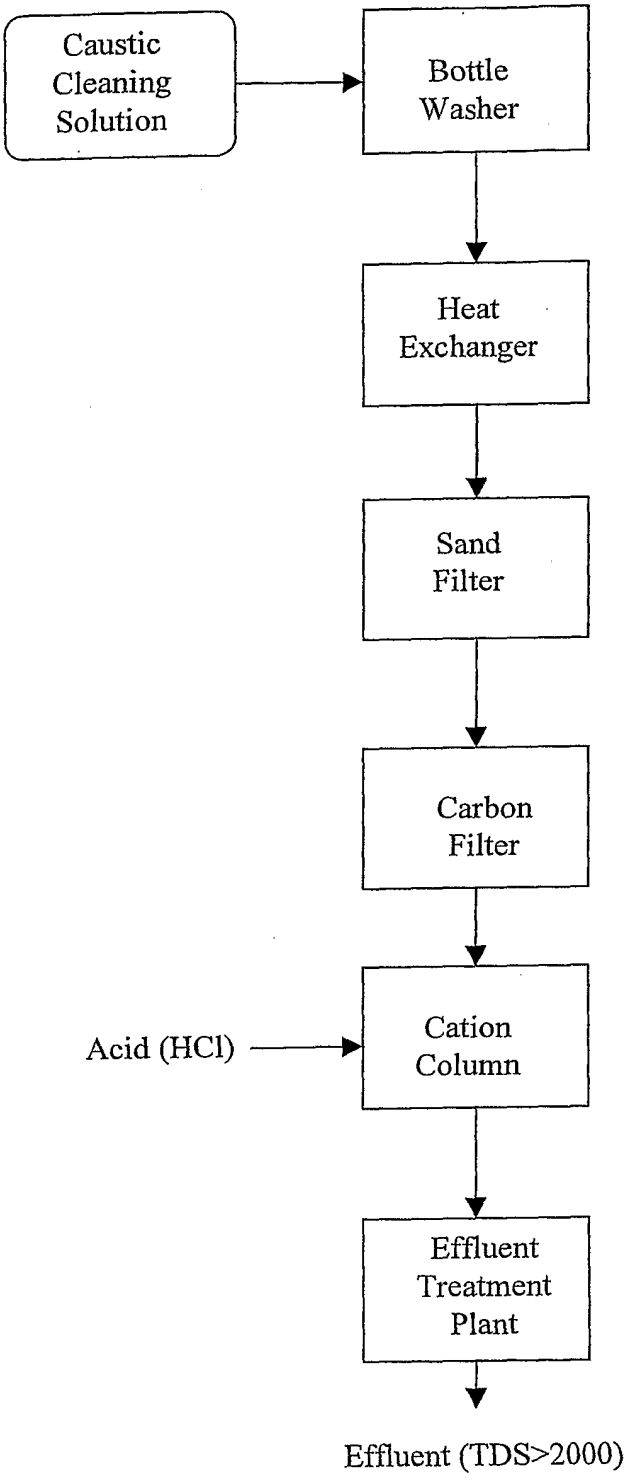
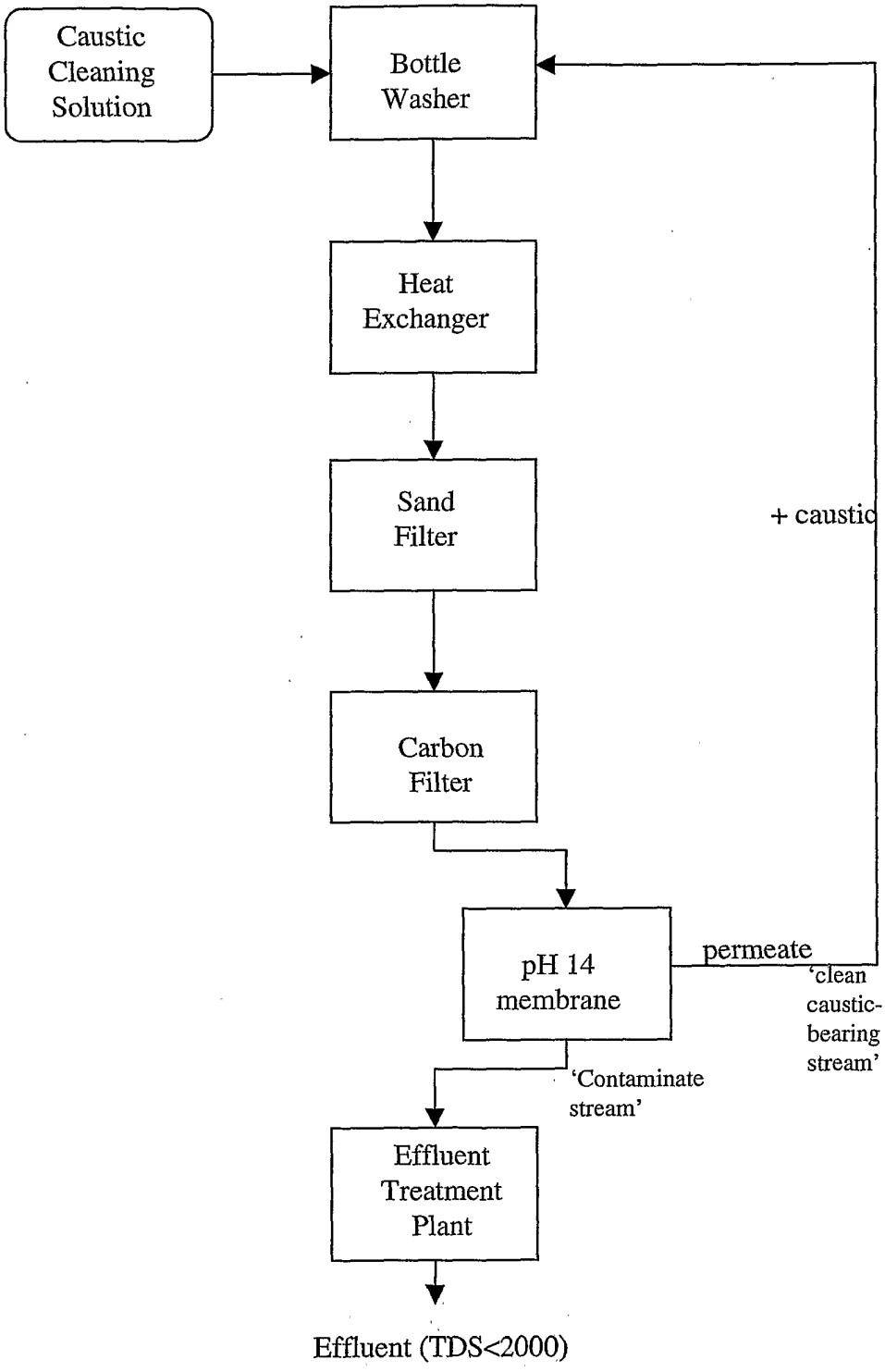

Caustic Cleaning Solution
Bottle Washer
Heat Exchanger
Sand Filter
Carbon Filter
Acid (HCl)
Cation Column
Effluent Treatment Plant
Effluent (TDS>2000)

Figure 2


Caustic Cleaning Solution
Bottle Washer
Heat Exchanger
Sand Filter
+ caustic
Carbon Filter
pH 14 membrane
permeate
'clean caustic-bearing stream'
'Contaminate stream'
Effluent Treatment Plant
Effluent (TDS<2000)

INTERNATIONAL SEARCH REPORT

PCT/GB 03/03457

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C02F1/44 B08B3/14 C23G1/36

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

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 C02F B01D C23G C01D B08B

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

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

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 0 551 245 A (FILTROX WERK AG) 14 July 1993 (1993-07-14) abstract; claims 1-11; figures page 2, line 1 -page 4, line 47 page 5, line 39 - line 43 page 5, line 53 - line 54	1-4,7-17
Y		6
A		5

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[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

° Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

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Date of the actual completion of the international search	Date of mailing of the international search report
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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

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