INSTRUCTIONS
(a) If Convention application insert "Convention"

# 600689

(a) Convention

Our Case: P30,095

AUSTRALIA

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(b) Delete one

## APPLICATION FOR A (b) STANDARD/~~PETTY~~ PATENT

APPLICATION ACCEPTED AND AMENDMENTS ALLOWED 18.6.90

(c) Insert FULL name(s) of applicant(s)

I/We (c)

PARKER CHEMICAL COMPANY

(d) FULL address(es) of applicant(s)

of (d)

32100 Stephenson Highway
Madison Heights, Michigan 48071
UNITED STATES OF AMERICA

LODGED AT SUB-OFFICE 23 DEC 1986 Melbourne

(e) Delete one

hereby apply for the grant of a (e) Standard/Petty Patent for an invention entitled

(f) TITLE of invention

(f) PROCESS FOR CLEANING ALUMINUM

(g) "complete" "provisional" "petty patent"

which is described in the accompanying (g) complete specification.

(*Note: The following applies only to Convention applications*)

Details of basic application(s)

(h) number, country and date for each application

| Application No. | Country | Filing Date |
|---|---|---|
| 820,869 | UNITED STATES OF AMERICA | Jan. 21, 1986 |
| 900,229 | UNITED STATES OF AMERICA | Aug. 25, 1986 |

LODGED AT SUB-OFFICE 23 DEC 1986 Melbourne

FEE STAMP TO VALUE OF $295 ATTACHED
MAIL OFFICER

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LODGED AT SUB-OFFICE 23 DEC 1986 Melbourne

(i) date of signing

Dated (i) 23 December, 1986

(j) Signature of applicant(s) or body (see headnote) seal, if any

(k) signature witnessed

(j) PHILLIPS ORMONE & FITZPATRIC
Attorneys for:
PARKER CHEMICAL COMPANY

(k)

LODGED AT SUB-OFFICE 23 DEC 1986 Melbourne

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# AUSTRALIA

*Patents Act*

Our Case P30,095

## DECLARATION FOR A PATENT APPLICATION

▼ **INSTRUCTIONS**
(a) Insert "Convention" if applicable
(b) Insert FULL name(s) of applicant(s)

In support of the (a) Convention application made by
(b)

PARKER CHEMICAL COMPANY

(c) Insert "of addition" if applicable
(d) Insert TITLE of invention

(hereinafter called "applicant~~s~~) for a patent (c) for an invention entitled (d)

"PROCESS FOR CLEANING ALUMINUM"

(e) Insert FULL name(s) AND address(es) of declarant(s) (See headnote*)

I/~~We~~ (e) Arthur E. Kluegel, Assistant Secretary of Parker Chemical Company, of 32100 Stephenson Highway, Madison Heights, Michigan 48071, United States of America

do solemnly and sincerely declare as follows:

1. ~~I am/We are the applicant(s).~~

*(or, in the case of an application by a body corporate)*

1. I am/~~We are~~ authorized to make this declaration on behalf of the applicant(~~s~~).

2. ~~I am/We are the actual inventor(s) of the invention.~~

*(or, where the applicant(s) is/are not the actual inventor(s))*

(f) Insert FULL name(s) AND address(es) of actual inventor(s)

2. (f) Thomas H. Fick, of 29225 Ursuline, St. Clair Shores, MI 48081, United States of America; Samuel T. Farina, of 35426 Rutherford, Mt. Clements, MI 48043, United States of America; and Peter F. King, of 26500 Orchard Lake Road, Farmington Hills, MI 48018, United States of America

(g) Recite how applicant(s) derive(s) title from actual inventor(s) (See headnote**)

~~is~~/are the actual inventor(s) of the invention and the facts upon which the applicant(~~s~~) is/~~are~~ entitled to make the application are as follows:
(g)

Applicant is the assignee of the actual inventors.

**(Note:** *Paragraphs 3 and 4 apply* **only** *to Convention applications)*

(h) Insert country, filing date, and basic applicant(s) for the/or EACH basic application

3. The basic application(s) for patent or similar protection on which the application is based ~~is~~/are identified by **country, filing date, and basic applicant(s)** as follows:
(h)

United States of America 21 January, 1986
Thomas H. Fick; Samuel T. Farina; Peter F. King.

United States of America 25 August, 1986
Thomas H. Fick; Samuel T. Farina; Peter F. King.

4. The basic application(s) referred to in paragraph 3 hereof ~~was~~/were the first application(s) made in a Convention country in respect of the invention the subject of the application.

(k) Insert PLACE of signing
(l) Insert DATE of signing
(m) Signature(s) of declarant(s)

Note: No legalization or other witness required

Declared at (k) Madison Heights, Michigan

Dated (l) January 21, 1987

(m) [signature]

Arthur E. Kluegel
Assistant Secretary
Parker Chemical Company

To: The Commissioner of Patents

P18/7/78

DF:DW

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# (12) PATENT ABRIDGMENT (11) Document No. AU-B-66882/86
# (19) AUSTRALIAN PATENT OFFICE (10) Acceptance No. 600689

(54) Title
CLEANING ALUMINUM

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(74) Attorney or Agent
PHILLIPS,ORMONDE & FITZPATRICK

(56) Prior Art Documents
AU 68678/87 C23G 1/12 1/22
AU 48590/85 C23G 1/22
US 4270957

(57) Claim

1. A process for cleaning aluminum container surfaces to remove aluminum fines and residual organic contaminants on the surfaces thereof, said process comprising the steps of:

(i) contacting the aluminum container surface with an aqueous alkaline cleaning solution for a period of time sufficient to remove substantially all of the aluminum fines and organic contaminants on the surface thereof; and thereafter

(ii) contacting the aluminum container surface with at least one acidulated water-based rinse solution at a pH below 2.5 to neutralize and remove any residual alkaline cleaner thereon and any oxide film on the surface formed during step (i).

21. A process for cleaning aluminum container surfaces to remove aluminum fines and residual organic contaminants on the surfaces thereof, said process comprising the steps of:

(i) contacting the aluminum container surface with an aqueous alkaline cleaning solution for a period of time sufficient to remove substantially all of the aluminum fines and organic contaminants on the surface thereof, and thereafter,

(ii) contacting the aluminum container surface with at least one acidulated water-based rinse solution containing free-fluoride and/or phosphate ions present in an amount effective to accelerate the removal of any oxide film on the surface of the aluminum container at a pH less than 6 and for a period of time in consideration of the temperature of said acidulated rinse solution sufficient to neutralize and remove any residual alkaline cleaner thereon and to substantially reduce any oxide film on the aluminum surface.

AUSTRALIA 600689

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# COMPLETE SPECIFICATION

(ORIGINAL)

Class | Int. Class

Application Number: 66882/86

Lodged:

Complete Specification Lodged:

Accepted:

Published:

Priority

Related Art:

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APPLICANT'S REF.: P30,054

Name(s) of Applicant(s): PARKER CHEMICAL COMPANY

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UNITED STATES OF AMERICA

Actual Inventor(s): THOMAS H. FICK,
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Complete Specification for the invention entitled:

PROCESS FOR CLEANING ALUMINUM

The following statement is a full description of this invention, including the best method of performing it known to applicant(s):

# PROCESS FOR CLEANING ALUMINUM

## BACKGROUND OF THE INVENTION

The present invention broadly relates to an improved process for cleaning aluminum surfaces, and more particularly, to a process employing a sequential cleaning cycle including a primary alkaline cleaning solution for effecting a removal of organic contaminants and aluminum fines from the surfaces of the containers and to further enhance the mobility of the containers facilitating their transport in high-speed can lines having a capacity in excess of about 1,000 cans per minute. The process of the present invention is particularly adaptable for cleaning drawn and ironed aluminum container bodies of the types employed in the packaging of foodstuffs and beverages. The cup-shaped and dished integral bottom of such container bodies, because of their configuration, are conducive to entrapment of the various cleaning and rinse solutions during the cleaning cycle which has in some instances resulted in an objectionable localized staining of the surfaces thereof during line stoppages during the cleaning process.

It has previously been discovered that by employing an aqueous alkaline cleaning solution of a controlled composition as described in ~~pending~~ U.S. Patent 4,599,116, ~~Application Serial No. 669,491,~~ filed November 8, 1984, and entitled "Alkaline Cleaning Process", an elimination of such localized objectionable staining could be achieved providing for clean aluminum containers of commercially satisfactory quality. It was also discovered, in accordance with the teachings of the aforementioned U.S. patent application, that an improvement in the mobility of such cleaned containers could be enhanced by subjecting the containers to a conventional conversion coating treatment following the cleaning and rinsing steps. Such increased mobility is important for effecting rapid transfer of such containers through the conveyorized processing lines without incurring jamming and disruption of the feed of the containers to subsequent processing steps such as lacquering, printing, decorating, and the like. While an improvement in can mobility has been achieved by the application of such a conversion coating, the mobility of such containers in high-speed can processing lines of a production capacity in excess of 1,000 cans per minute to as high as about 1,500 cans per minute has been less than optimum.

In accordance with the present invention, it has been discovered that by using an acidulated water rinse treatment following the alkaline cleaning treatment and prior to any subsequent optional conversion coating treatment, a substantial increase in the mobility of such containers is achieved further enhancing their processing through subsequent stages.

SUMMARY OF THE INVENTION

The benefits and advantages of the present invention are achieved by a sequential process for cleaning and treating aluminum surfaces, and particularly aluminum containers to remove aluminum fines and residual organic contaminants including die lubricants remaining on the surfaces thereof following the several manufacturing steps including ~~the drawing and ironing of the containers into a container body. The process in accordance with its preferred embodiments includes the steps~~

the drawing and ironing of the containers into a container body.

According to the present invention there is provided a process for cleaning aluminum container surfaces to remove aluminum fines and residual organic contaminants on the surfaces thereof, said process comprising the steps of:

(i) contacting the aluminum container surface with an aqueous alkaline cleaning solution for a period of time sufficient to remove substantially all of the aluminum fines and organic contaminants on the surface thereof; and thereafter

(ii) contacting the aluminum container surface with at least one acidulated water-based rinse solution at a pH below 2.5 to neutralize and remove any residual alkaline cleaner thereon and any oxide film on the surface formed during step (i).

The present invention also provides a process for cleaning aluminum container surfaces to remove aluminum fines and residual organic contaminants on the surfaces thereof, said process comprising the steps of:

(i) contacting the aluminum container surface with an aqueous alkaline cleaning solution for a period of time sufficient to remove substantially all of the aluminum fines and organic contaminants on the surface thereof, and thereafter,

(ii) contacting the aluminum container surface with at least one acidulated water-based rinse solution containing free-fluoride and/or phosphate ions present in an amount effective to accelerate the removal of any oxide film on the surface of the aluminum container at a pH less than 6 and for a period of time in consideration of the temperature of said acidulated rinse solution sufficient to neutralize and remove any residual alkaline cleaner thereon and to substantially reduce any oxide film on the aluminum surface.

The process in accordance with its preferred embodiments includes the steps



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of contacting the aluminum containers with a preferred acidic aqueous pre-wash solution for a period of time sufficient to remove a portion of the residual aluminum fines and organic contaminants on the surfaces thereof. Thereafter, the pre-washed containers are contacted with an aqueous primary alkaline cleaning solution containing an alkalinity agent present in an amount to remove aluminum fines from the surfaces of the containers in further combination with a complexing agent, one or a combination of surfactants to remove the organic soils on the surfaces of the container and optionally, an antifoaming agent. Following the alkaline cleaning step, the cleaned containers are thereafter subjected to one or a plurality of counterflowed highly acidulated water rinses, with or without a prior intervening water rinse, to effect the neutralization and removal of residual alkaline cleaner thereon of which at least one rinse stage contains an acidity agent present in an amount sufficient to provide a pH of less than about 6, preferably below about 5, depending on whether or not an accelerating agent is present in the acidulated rinse solution. The acidulated water rinse, depending on the temperature and time of contact, may optionally and preferably contain free fluoride and/or phosphate ions to accelerate the oxide and stain removal from the aluminum container surfaces. The acid rinsed containers are preferably further water rinsed with a solution at substantially neutral pH, whereafter, the rinsed containers are optionally subjected to a conversion treatment to impart a desired conversion coating thereon. Following the conversion coating, if applied, the containers are again subjected to one or a plurality of water rinses whereafter they are dried and can thereafter be further processed such as by lacquering, painting, decorating and the like prior to being filled with appropriate foodstuffs or beverages.

The use of the acidulated water rinse stage following the alkaline cleaning step has been found to markedly increase the mobility of the containers believed to occur as a result of a removal of an oxide film formed on the container surfaces during the alkaline cleaning step as well as removing any staining of the surfaces of the containers and greatly enhancing the transferability of the containers such as by rolling and/or sliding through the conveyorized transfer lines and chutes.

Additional benefits and advantages of the present invention will become apparent upon a reading of the description of the preferred embodiments taken in conjunction with the specific examples provided.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

In accordance with the practice of the process of the present invention, and with particular emphasis on the cleaning of drawn and ironed aluminum containers, the aluminum containers are transferred from the body-making and trimming apparatus to a multiple stage high-speed cleaning apparatus to effect a removal of the residual body-forming lubricants and aluminum fines or smut formed on the surfaces of the containers during the manufacturing operation. The aluminum fines comprise minute particles of aluminum on the container surfaces and adhered thereto in combination with various lubricants and metal working compounds employed during the forming operations of the container.

The first stage of the cleaning cycle preferably comprises contacting the surfaces of the containers with an aqueous pre-wash solution, preferably an aqueous acidic pre-wash solution, to effect a removal of at least a portion of the fines and/or organic soils from the container surfaces thereby reducing a buildup of such contaminants in the succeeding primary alkaline cleaning stage.

The pre-wash solution is applied to the aluminum container surfaces at temperatures ranging from ambient (i.e. from about $60^{\circ}$ F) up to about $200^{\circ}$ F, and preferably at a temperature below about $150^{\circ}$ F, such as from about $90^{\circ}$ to about $130^{\circ}$ F. The pre-wash solution is contacted with the aluminum surfaces to be cleaned such as by flooding, immersion or spraying of which the latter constitutes the preferred method to assure uniform distribution of the pre-wash solution on both the interior and exterior surfaces of the container.

Following the pre-wash stage, the preliminarily cleaned aluminum containers are transferred directly to a primary alkaline cleaner stage incorporating an aqueous alkaline cleaning solution of a composition preferably as described in ~~pending~~ U.S. Patent 4,599,116 ~~Application Serial No. 669,491~~ the substance of which is incorporated herein by reference. Typical of suitable aqueous alkaline cleaning compositions are those containing an alkalinity agent present in an amount to achieve satisfactory removal of residual aluminum fines on the surfaces of the containers without incurring undesirable etching of the surfaces. Generally, the pH of the alkaline cleaning solution ranges from at least about 11 up to about 13. The alkalinity agent may comprise an alkali metal hydroxide and/or alkali metal carbonate in further combination with a suitable complexing agent present in an amount effective to complex at least some of the metal ions present in the cleaning solution which otherwise tend to form solution insoluble precipitates. The alkaline cleaning solution can optionally further contain a foam-suppressant agent of any one of the types conventionally employed which is utilized in consideration of the types and concentration of the surfactants employed. The foam suppressant agent is used at a level sufficient to prevent undesirable foaming of the cleaning solution particularly when it is applied by spray application.

In accordance with a preferred practice, the alkaline cleaning solution is controlled at a pH ranging from about 11 up to about 13 with a pH of from about 11.5 to about 12.5 being preferred. In order to achieve an alkalinity within the foregoing range, the alkalinity agent such as a mixture of sodium hydroxide and sodium carbonate is employed at concentrations of from about 0.05 up to about 10 g/1.

Complexing agents suitable for use in the alkaline cleaning solution comprise sugar acids as well as salts thereof such as, for example, sodium gluconate, sodium citrate, sodium tripolyphosphate, as well as other acids including glucoheptanoic acid, tartaric acid, EDTA and the like as well as the bath soluble and compatible salts and mixtures thereof.

The alkaline cleaning solution may further contain ~~as an essential ingredient~~ at least one or a combination of surfactants which are usually selected from the group comprising hydrocarbon alkoxylated surfactants which are characterized as individually or in their blended combination as having a Hydrophile-Lipophile Balance (HLB ratio), i.e. the balance of the size and strength of the hydrophilic (water-loving or polar) and the lipophilic (oil-loving or non-polar) groups of the molecule within an HLB ratio of at least about 12, preferably at least about 12 to about 15. While other surfactants can be employed to provide for effective cleaning of the alkaline cleaning solution, it has been found that employing surfactants characterized by the foregoing HLB ratios substantially reduces or eliminates a tendency of white staining on the surfaces of the aluminum container occasioned by line stoppages which frequently occur in high-capacity, high-speed container washers.

Such line stoppages may range from about one-half minute to as long as about one hour and the presence of residual cleaning solution on the container surfaces has occasioned such white-staining problems. By employing surfactants of the appropriate HLB ratio, such white-staining has been substantially eliminated.

The aqueous alkaline cleaning solution can also be applied, as in the case of the acidic pre-wash solution, by flooding, immersion and preferably by spray application for a period of time sufficient to effect a cleaning of the surfaces thereof. Generally, the aqueous alkaline cleaning solution is employed at moderate temperatures below about $150^{\circ}$F to about ambient temperature with temperatures of from about $90^{\circ}$ to about $130^{\circ}$F being preferred.

Following the aqueous alkaline cleaning stage, the cleaned containers are transferred to a water rinse stage, preferably a multiple stage water rinse section of the conveyorized washer. In accordance with the process as described in ~~pending~~ U.S. Patent 4,599,166 ~~Application Serial No. 669,491,~~ it was discovered that by maintaining the pH of the water rinse solution at a level below about pH 7.5, a further elimination of any tendency to form brown stains on the container bodies was achieved during the rinsing stage. As demonstrated in the prior pending application, if the pH of the aqueous rinse stage rises to a level above about 7.5 as a result of carry-over of alkaline cleaning solution into the water rinse stage, brown staining of the aluminum container surfaces occurs particularly when line stoppages occur in the rinsing stage.

It has now been further discovered that by increasing the acidity of the water rinse solution employed in the rinse stage following the primary alkaline cleaning step, with or without an intervening water rinse step, not only brown staining is prevented, but a further substantial improvement in the mobility of the cleaned aluminum containers is obtained. It is believed that this increased mobility is a result of the substantial reduction of or removal of an aluminum oxide film formed on the aluminum container surfaces during the alkaline cleaning step. The substantial reduction of the aluminum oxide film on the aluminum surfaces also effects a substantial or complete removal of objectional stains that may have formed on the aluminum container surfaces during and following the alkaline cleaning stage. Because of this, the containers following the alkaline cleaning stage and prior to the acidulated water rinse stage can be subjected to a conventional tap water rinse to remove a substantial portion of the residual alkaline cleaner from the surfaces thereof prior to the acidulated water rinse stage. Any staining occurring in the tap water rinse stage, which may become somewhat alkaline because of drag-in, as a result of line stoppages, can be substantially and/or completely removed in the following acidulated water rinse stage producing containers of acceptable commercial quality. In order to achieve such further improvement, it has been found that the acidulated water rinse solution should be at an acid pH low enough for the specific contact time and rinse solution temperature, method of application and concentration, if any, of accelerating agents to achieve removal of substantially all stains formed during any prior stages. The acidulated rinse solution should be at a pH of less than about 6, preferably less than about 5, in the presence of free-fluoride and/or phosphate ions and below about 2.5, preferably below about 2, in the absence of free-fluoride and/or phosphate ions. When tertiary stage acidic water rinse section is employed, the second-recirculating stage of the three-stage water rinse should contain the rinse solution at the required maximum pH. The water rinse solution from the third or last rinse stage can conveniently be counterflowed to the preceding stages such as in a three-stage water rinse section. The acidulated water rinse solution is applied to the containers in the same manner and at the same temperatures employed for the pre-wash and alkaline cleaning solutions. Acidulation of the water rinse solution can be achieved by employing any one or combinations of commonly available organic and inorganic acids of which sulfuric and/or hydrofluoric acids constitute the preferred materials. The presence of free-fluoride through the addition of hydrofluoric acid or simple or complex fluoride and soluble salts may also be employed in amounts sufficient to enhance mobility or improve stain suppression/removal.

The effectiveness of the reduction of oxide film to an acceptable level in the acidulated water rinse stage is related to the temperature employed and the duration of contact of the acidulated rinse solution with the container surface. The method of application of the acidulated rinse solution also constitutes a variable with spray application at high pressure (high volume) constituting the preferred practice. In commercial can washers of the general types presently employed, pre-wash contact times of about 20 seconds up to about one minute are usual while alkaline cleaner contact times generally range from about 10 seconds up to about one minute. Acidulated water rinse stages have normal contact times ranging from about 10 up to about 30 seconds. Under some manufacturing conditions, the can washers will operate at one-half speed for certain time intervals under which conditions the aforementioned contact times are doubled.

While mineral acids such as sulfuric acid itself is effective to reduce the oxide film when employed at temperatures approaching 200°F, such elevated temperatures are energy intensive, and for this reason, temperatures below about 150°F are preferred. It has been found, however, that at acidulated water rinse temperatures below about $160^{\circ}$F employing usual contact times, sulfuric acid itself is only marginally effective to remove the necessary quantity of oxide film and any prior staining that may have occurred on the container surfaces. Accordingly, when lower acidulated water rinse temperatures are employed, such as from about $90^{\circ}$F to about $130^{\circ}$F, the addition of an effective amount of free fluoride and/or phosphate ions to accelerate the oxide film removal properties of the acidulated rinse solution has been found necessary and preferred practice under conventional commercial operations. Of the foregoing, free-fluoride constitutes the preferred material due to the relatively small quantities required to achieve the necessary acceleration in comparison to phosphate ions which must be added in amounts substantially higher than fluoride to achieve equivalent results. Generally, free-fluoride ions in amounts as low as 1 ppm provide for an increase in acceleration with amounts as high as 100 ppm or higher to as high as about 1,000 ppm being usable subject to environmental restrictions. Excessive free-fluoride concentrations, that is, above about 200 ppm under certain processing conditions have been observed to cause an undesirable etching of the aluminum container surface which detracts from the shiny metallic appearance of the surface. Because of this, the free-fluoride ion concentration is preferably controlled at a level below about 100 ppm. Generally, free-fluoride in amounts of less than about 40 ppm are satisfactory and preferred from both an economic and environmental standpoint.

The free-fluoride ions can be added as hereinbefore set forth to the acidulated water rinse solution as simple or complex fluorides and/or soluble salts of which hydrofluoric acid itself constitutes the preferred material.

In accordance with conventional practice, the cleaned and acidulated water rinsed containers may be subjected to a final third-stage-exit water flush-off rinse upon emerging from the acidulated rinse section, which serves to remove residual acidulated rinse solution therefrom, as well as supplying fresh make-up water to the rinse stage.

Following the water rinsing of the cleaned aluminum containers, if further mobility enhancement is desired and/or an improvement in the pasteurization characteristics of the filled containers, one may optionally subject the containers to a conversion treatment such as by employing treating solutions based on chromium phosphate or titanium or zirconium with or without tannin. Exemplary of such conversion coatings suitable for use in the present process are those described in U.S. Patent Nos. 4,017,334; 4,054,466 and 4,338,140, the teachings of which are incorporated here by reference.

The cleaned and treated containers can thereafter be dried and subjected to the application of one or a plurality of sanitary lacquer coatings, decorative coatings, inks, and the like in accordance with conventional practice prior to the filling and sealing thereof with appropriate food stuffs or beverages.

In order to further illustrate the improved process of the present invention the following specific examples are provided. It will be understood that the examples are provided for illustrative purposes and are not intended to be limiting of the scope of the present invention as herein described and as set forth in the subjoined claims.

EXAMPLE 1

In order to demonstrate the effectiveness of the present process in improving can mobility in high-speed can processing lines, an experimental field test was conducted employing a multiple stage high-speed cleaning apparatus to effect a removal of residual body-making lubricants and aluminum fines from the surfaces of drawn and ironed aluminum containers. The multiple stage washer contained three primary stages in which Stage 1 comprised an aqueous prewash employing a solution at a pH of about 10.5; Stage 2 comprised an aqueous alkaline primary cleaning solution of the type previously described at a pH of about 11.9; an aqueous acidulated water rinse stage controlled at a pH of about 2.5 which was followed by a tap water flush-off rinse stage prior to transfer to a conversion treatment stage operated at a pH of from about 2.8 to about 3.2. Following the conversion treatment, the containers were water rinsed followed by a deionized water rinse and were thereafter oven dried. Following drying, the cans were transferred by conveyorized transfer lines and chutes to a printer at a nominal rate of about 980 to about 1,000 cans per minute. Under the foregoing operating conditions, the mobility of the cans was acceptable providing for high-speed printing.

By reducing the acidity in Stage 3 of the acidulated rinse solution from an operating pH of about 2.5 to a pH of about 5, can mobility was significantly reduced whereby the capacity of the printer had to be reduced to a rate of 710 cans per minute to provide satisfactory operation. When the acidulated rinse solution was again further acidified to restore its pH at a level of about 2.5, the mobility of the cans improved and the rate of printing was also restored to a level of about 980 to about 1,000 cans per minute.

The benefits of applying a conversion treatment to the aluminum containers following the acidulated rinse step in accordance with a preferred practice was also demonstrated by omitting the conversion treatment for a 24 hour test period. Can mobility was reduced apparently due to an oxide build-up on the conveyorized rails and chutes such that the rate of printing had to be reduced to a level of about 820 cans per minute. When the conversion treatment was restored, can mobility was again restored and the printing rate returned to normal.

## EXAMPLE 2

In order to demonstrate the effectiveness of free-fluoride ions to accelerate the removal of oxide film from aluminum container surfaces, aluminum cans were cleaned in a laboratory can washer by spray application employing 19 liters of cleaning solution. The cleaning solution consisted of sodium hydroxide dissolved in water to provide a pH of 12.1. The cleaning solution was heated to 120 $^{o}$F and spray applied to the aluminum containers for a period of one minute. The containers were inverted so that the concave dome retained a residual quantity of cleaning solution which was allowed to stand on the container for a period of one-half hour. The containers were thereafter subjected to a tap water rinse. An objectionable brown stain was present in the dome of the container along the periphery of residual alkaline cleaning solution that was retained therein.

An acidulated water rinse solution totaling 19 liters was prepared containing one gram per liter of tartaric acid which was adjusted to a pH of 1.91 by sulfuric acid. The acidulated rinse solution at a temperature of 120 $^{o}$F was applied for one minute to the stained aluminum containers whereafter the containers were water rinsed and inspected for stain removal. A rating system was employed in which a rating of 1 indicates no stain removal while a rating of 5 indicates a complete stain removal. An inspection of the aluminum container revealed a stain rating of 1 indicating no stain removal.

## EXAMPLE 3

To the acidulated water rinse solution as described in Example 2, 0.5 milliliters of 50 percent hydrofluoric acid was added to the 19 liters of rinse solution. An acidulated water rinsing of stained aluminum containers was repeated at a temperature of 120 °F for a period of one minute. Following the acidulated water rinsing, the containers were water rinsed and inspected. The stain rating of the aluminum containers containing the hydrofluoric acid was increased to 4.8 indicating almost complete stain removal.

## EXAMPLE 4

The interrelationship of acidity, free-fluoride concentration, temperature and time of the acidulated water rinse treatment relative to the effectiveness of stain removal was evaluated by forming an acidulated water rinse solution containing sulfuric acid in variable amounts to provide the desired pH. Stained aluminum containers prepared as previously described in connection with Example 2 were acid rinsed employing such solutions at variable temperatures of 90 °F and 120 °F for time periods of 15 seconds and one minute to determine the concentration of free-fluoride present to provide a stain rating of 5. The results obtained are set forth in the following table:

### TABLE

ppm Free-Fluoride Required For Stain Rating of 5

| | pH 3 | | pH 2.14 | pH 1.7 | pH 0.4 | |
|---|---|---|---|---|---|---|
| TEMPERATURE, | 90 °F | 120 °F | 120 °F | 120 °F | 90 °F | 120 °F |
| TIME, 15 sec. | 171 | 68 | 64 | 69 | 190 | 109 |
| TIME, 60 sec. | 68 | 23 | 13 | 18 | — | — |

The results as set forth in the foregoing table indicates that as temperature increases or time incrᵔases, the concentration of free-fluoride in ppm to effect a rating of 5 decreases. As the pH of the acidulated rinse solution decreases below a pH of about 2, as evidenced by the data provided for the acidulated rinse solution at a pH of 0.4, the concentration of free-fluoride increases in comparison to that required at a pH of from about 2 to about 3. The foregoing test data indicates that when moderate acidulated rinse solution temperatures are employed and are accelerated by employing free-fluoride ions, the optimum pH for removing brown stains ranges from about 1.5 to about 2.5.

EXAMPLE 5

The interrelationship of acidity, solution temperature and time of contact at a constant free-fluoride concentration was evaluated relative to the effectiveness of stain removal by forming an acidulated water-based rinse solution containing 1,000 ppm free-fluoride added as sodium fluoride and containing sulfuric acid in variable amounts to provide the desired pH. Separate groups of drawn and ironed aluminum containers were processed through a conveyorized laboratory pilot can washer including a first cleaning stage employing an alkaline cleaning solution containing sodium hydroxide, a chelating agent and a surfactant at a pH ranging from about 12.0 to about 12.2 at a temperature of 130 $^{o}$F for a period of 45 seconds by spray application. Following the alkaline cleaning stage, the containers were transferred into a second tap-water rinse stage with the rinse water turned off and the cleaned containers were permitted to stand for a period of 20 minutes containing alkaline cleaner in the dome sections thereof simulating a line stoppage. Following the 20 minute dwell, one can was removed and the stain in the dome section was inspected. The remainder of the containers were retained in stage two whereafter the tap-water sprays were turned on for a period of 15 seconds at room temperature and the water rinsed containers were thereafter transferred to a third-stage containing an acidulated highly accelerated rinse solution containing 1,000 ppm free-fluoride. A series of tests were conducted at each pH level commencing at a pH of 7 at two different temperatures and at two different contact times. The temperatures selected were 90 $^{\circ}$F and 120 $^{\circ}$F and the spray contact times were selected at 15 seconds and 60 seconds. Each series of tests started employing the longest contact time at the highest temperature to evaluate the effectiveness of stain removal compared to the container removed from the second-stage prior to tap-water rinsing. If only a marginal improvement was obtained under such conditions, the remaining tests of that series employing lower temperatures and/or lower contact times were not run in anticipation that the results would be less favorable than those obtained at the higher temperature and contact time condition.

Following the accelerated acidulated third rinse stage, the containers were transferred to a fourth stage containing a deionized water rinse whereafter the containers were dried and the stain remaining in the dome section thereof was compared to the control sample removed from the second tap-water rinse stage. In accordance with the rating system described in Example 4, a stain rating of 1 was assigned to those containers in which no perceptible stain removal was obtained while a stain rating of 5 was assigned to test samples exhibiting a subtantially complete stain removal. In addition to an inspection of the degree of stain removal, the aluminum container surfaces were also inspected for undesirable etching which in some commercial operations would result in a rejection of such containers as unacceptable. The results of the five groups of separate test runs are summarized in the following table including an indication as signified by the letter "E" whether the surfaces were highly etched.

TABLE

| | pH 7 | | pH 6 | | pH 5 | | pH 4.5 | | pH 4 | |
|---|---|---|---|---|---|---|---|---|---|---|
| Temp., °F. | 90 °F | 120 ° | 90 ° | 120 ° | 90 ° | 120 ° | 90 ° | 120 ° | 90 ° | 120 ° |
| Time, 15 sec. | — | — | — | — | — | 2 | 5 | 5 | 5 | 5E* |
| Time, 60 sec. | — | 1 | — | 1 | 2 | 5 | 5 | 5 | 5E | 5E |

*E = undesirable etching of surface

It is apparent from the data as set forth in the foregoing Table under the specific conditions employed, that the acidulated rinse solution at a pH of about 7 was ineffective to remove any stain from the dome of the container employing a temperature of 120 °F and a contact time of 60 seconds. Accordingly, the remaining three tests at pH 7 were not run in anticipation that the results would even be poorer. Similarly, at a pH of 6, the highly accelerated acidulated rinse solution was ineffective to remove any appreciable stain employing a solution temperature of 120 °F and a contact time of 60 seconds. Accordingly, the remaining three tests of that group were not conducted. At a pH of 5, however, at a temperature of 120 °F and at a contact time of 60 seconds, the highly accelerated acidulated rinse solution was effective to remove substantially all of the stain on the containers. A stain rating of 2 was obtained when the contact time was reduced to 15 seconds or when the solution temperature was reduced to 90 °F. In view of these results, the test at 90 °F and 15 second contact time was omitted.

At a pH of 4.5, stain ratings of 5 were obtained under all of the temperature and contact conditions specified. As the pH was further reduced to 4, undesirable etching was observed except for the test conducted at $90^{o}F$ and 15 second contact time.

It is apparent from the relationship of the results as set forth in the foregoing Table, that optimum stain removal without experiencing undesirable etching can be achieved by an appropriate correlation of the pH, temperature, contact time, concentration of the accelerating agent, and manner of application of the acidulated rinse solution in accordance with routine testing for any specific commercial installation.

While it will be apparent that the preferred embodiments of the invention disclosed are well calculated to fulfill the objects above stated, it will be appreciated that the invention is susceptible to modification, variation and change without departing from the proper scope or fair meaning of the subjoined claims.

The claims defining the invention are as follows:

1. A process for cleaning aluminum container surfaces to remove aluminum fines and residual organic contaminants on the surfaces thereof, said process comprising the steps of:

(i) contacting the aluminum container surface with an aqueous alkaline cleaning solution for a period of time sufficient to remove substantially all of the aluminum fines and organic contaminants on the surface thereof; and thereafter

(ii) contacting the aluminum container surface with at least one acidulated water-based rinse solution at a pH below 2.5 to neutralize and remove any residual alkaline cleaner thereon and any oxide film on the surface formed during step (i).

2. The process as defined in claim 1, including the further step of contacting the aluminum container surface with an aqueous pre-wash solution for a period of time sufficient to remove at least a portion of the aluminum fines and residual organic contaminants on the surface thereof prior to the step of contacting the aluminum container surface with the aqueous alkaline cleaning solution.

3. The process as defined in claim 1 or claim 2 in which at least one said acidulated water rinse solution is at a pH of about 2.

4. The process as defined in any one of claims 1 to 3 in which the step of contacting the aluminum container surface with the at least one acidulated water-based rinse solution is performed in a plurality of contact stages with the second downstream stage being of a pH of below 2.5.

5. The process as defined in claim 4 in which a portion of the at least one acidulated water-based rinse solution in the last downstream stage is counterflowed to the adjacent upstream stage.

6. The process as defined in any one of claims 1 to 5 including the further step of controlling the pH of the at

least one acidulated water-based rinse solution at a level below 2.5 by the addition of an acidity agent thereto.

7. The process as defined in claim 6 in which said acidity agent comprises at least one acid selected from the group consisting of sulfuric acid and hydrofluoric acid.

8. The process as defined in any one of claims 1 to 7 including the further step of controlling the temperature of the at least one acidulated water-based rinse solution within a range of $60^{O}$ to $200^{O}F$.

9. The process as defined in any one of claims 1 to 7 including the further step of controlling the temperature of the at least one acidulated water-based rinse solution at a temperature below $150^{O}F$.

10. The process as defined in any one of claims 1 to 7 including the further step of controlling the temperature of the at least one acidulated water-based rinse solution within a range of $90^{O}$ to $130^{O}F$.

11. The process as defined in any one of claims 1 to 10 including the further step of contacting the aluminum container surface with a flush-off water rinse immediately following the step of contacting the aluminum container surface with the at least one acidulated water-based rinse solution.

12. The process as defined in any one of claims 1 to 11 including the further step of controlling the pH of said aqueous alkaline cleaning solution within a range of 11 to 13.

13. The process as defined in any one of claims 1 to 12 in which the step of contacting the aluminum container surface with the at least one acidulated water-based rinse solution is performed by spray application.

14. The process as defined in any one of claims 1 to 13 including the further step of contacting the acidulated water-based rinsed aluminum container surface with a treating solution to apply a conversion coating thereon.

15. The process as defined in any one of claims 1 to 14 including the further step of water rinsing the cleaned

and acidulated water-based rinsed aluminum container surface.

16. The process as defined in any one of claims 1 to 15 including the further step of drying the cleaned and rinsed aluminum container surface.

17. The process as defined in any one of claims 1 to 16 wherein the acidulated water-based rinse solution contains soluble fluoride salts.

18. The process as defined in any one of claims 1 to 17 including the further step of contacting the aluminum container surface with an aqueous water rinse solution following the alkaline cleaning solution and prior to the at least one acidulated water-base rinse solution to remove at least a portion of the residual alkaline cleaner thereon.

19. The process as defined in any one of claims 1 to 18 in which the at least one acidulated water-based rinse solution contains fluoride ions in an amount of at least 1 ppm.

20. The process as defined in any one of claims 1 to 19 in which at least said one acidulated water-based rinse solution contains phosphate ions in an amount effective to accelerate the removal of oxide film from the aluminum containers.

21. A process for cleaning aluminum container surfaces to remove aluminum fines and residual organic contaminants on the surfaces thereof, said process comprising the steps of:

(i) contacting the aluminum container surface with an aqueous alkaline cleaning solution for a period of time sufficient to remove substantially all of the aluminum fines and organic contaminants on the surface thereof, and thereafter,

(ii) contacting the aluminum container surface with at least one acidulated water-based rinse solution containing free-fluoride and/or phosphate ions present in an amount effective to accelerate the removal of any oxide film on the surface of the aluminum container at a pH less than 6 and for a period of time in consideration of the temperature of said acidulated rinse solution sufficient to neutralize and remove any residual alkaline cleaner thereon and to substantially reduce any oxide film on the aluminum surface.

22. The process as defined in claim 21 in which the at least one acidulated water-based rinse solution contains free-fluoride ions in an amount of 1 to 1000 ppm.

23. The process as defined in claim 21 in which the at least one acidulated water-based rinse solution contains free-fluoride ions in an amount below 100 ppm.

24. The process as defined in claim 21 in which the at least one acidulated water-based rinse solution contains free-fluoride ions in an amount of 1 to 40 ppm.

25. The process as defined in claim 21 in which the at least one acidulated water-based rinse solution contains phosphate ions present in an amount effective to accelerate removal of any oxide film on the surface of the aluminum container.

26. The process as defined in any one of claims 21 to 25 in which at least one acidulated water-based rinse solution is controlled at a pH less than 5.

27. The process as defined in any one of claims 21 to 26 including the further step of contacting the aluminum container surface with an aqueous pre-wash solution for a period of time sufficient to remove at least a portion of the aluminum fines and residual organic contaminants on the surface thereof prior to the step of contacting the aluminum container surface with the aqueous alkaline cleaning solution.

28. The process as defined in any one of claims 21 to 27 including the further step of contacting the aluminum container surface with an aqueous water rinse solution following the alkaline cleaning solution and prior to the at least one acidulated water-base rinse solution to remove at least a portion of the residual alkaline cleaner thereon.

29. The process according to claim 1, substantially as

hereinbefore described with reference to any one of the examples.

30. The process according to claim 21, substantially as hereinbefore described with reference to any one of the examples.

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