

COMPOSITIONS AND PROCESSES FOR CONDITIONING
THE SURFACE OF FORMED METAL ARTICLES

This invention relates to compositions and processes for conditioning the surface of formed metal articles.

It is more particularly directed to compositions and processes that produce on such formed metal articles, e.g. aluminium cans, a conditioned surface that is substantially or entirely free from "water breaks" when wet, or in other words a surface over which any water present on the surface spreads spontaneously. More specifically this invention is concerned particularly with certain aqueous compositions, suitable for contacting formed metal surfaces to deposit thereon (after drying) a mobility-enhancing lubricant film, said compositions being protected against deterioration from the action of micro-organisms during storage and/or against foaming during use.

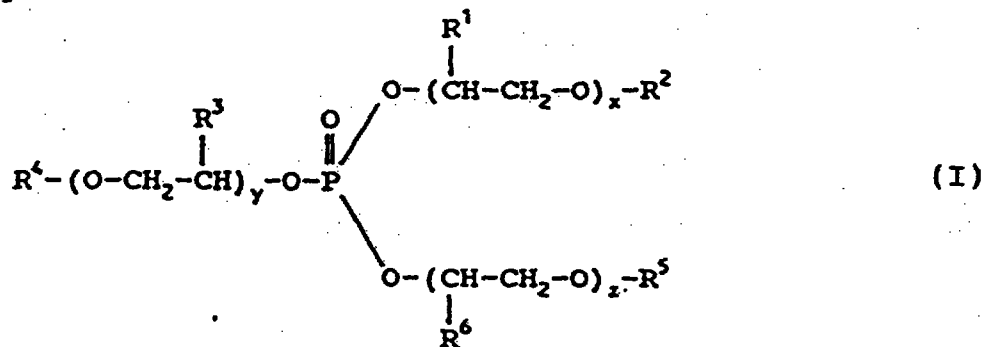
This invention stems from our continuing efforts to combat the problems that beset the high-speed production of aluminium beverage cans, as described in our United States Patent No. 4,859,351, and in that sense it is a development of and has some analogy with the procedures there described, though it should be emphasised that the present invention also in many ways is a clear departure from those known procedures, and capable of achieving distinctly better results.

We have found that the processes of the Examples of the aforesaid United States Patent No. 4,859,351 cannot readily

be operated in a way to inhibit bacterial growth and also that there can be problems created by foaming.

At this point it is convenient to note that in our co-pending Application No. 91-05316.5 (from which this Application has been divided, and therefore of even date herewith) we have described and claimed certain liquid, aqueous multi-component compositions which besides water comprise:

-(A) one or more water-soluble materials conforming to the general formula:



(wherein each of R^1 , R^3 and R^6 , which may be the same or different, is hydrogen or an alkyl group containing from 1 to 4 carbon atoms, each of x , y and z is zero or an integer from 1 to 25, and each of R^2 , R^4 and R^5 , which may be the same or different, is hydrogen or a monovalent cation or a monovalent fraction of a polyvalent cation or an alkyl, aryl or arylalkyl group containing from 1 to 20 carbon atoms, provided however that at least one of R^2 , R^4 and R^5 (i) is not hydrogen and (ii) has at least one alkoxy group interposed

between it and the phosphorus atom);

-(B) one or more water-soluble salts containing ions that include one or more Fe, Zr, Sn, Al and/or Ce atom(s); and

-(C) one or more water-soluble metal-etching compounds; as well as processes in which the surface of a previously-formed aluminium article, already de-greased and cleaned to remove aluminium fines and other solid contamination therefrom and thereafter water-rinsed, is treated by contact with such a liquid, aqueous multi-component composition.

By these means, as described in our aforesaid co-pending Application No. 91-05316.5, we have found that a formed metallic and especially aluminium surface, which has in a conventional manner been thoroughly cleaned and de-greased by sufficient contact with a water-based acid or alkaline cleanser, can be effectively and advantageously surface-conditioned so as to impart increased mobility, i.e. a low coefficient of static surface friction, to the surface when subsequently dried, without harming the reflectivity or printability of the thus-treated surface or the adherence of lacquer thereto.

It is one of the advantages of the compositions disclosed in our aforesaid co-pending Application No. 91-05316.5 that they may be used in the processes at a pH so

acidic that bacterial growth is inhibited, and resultant degradation thereby avoided. However, those multi-component compositions may be operated successfully over quite a wide range of pH values, not all of which will necessarily be inhibitory; and the previously-known compositions and processes typified by our aforesaid U.S. Patent No. 4,859,351 are not adequately resistant to biodegradation.

We have now found that the resistance to biodegradation of the compositions employed for this kind of purpose can be improved by including an effective amount of a biocide, most advantageously hydrogen peroxide. And we have also found that in the application of such compositions to bring them into contact with the aluminium or other metallic surface there can be problems created by foaming, which can be alleviated if the composition also includes an effective amount of an anti-foaming agent.

According to one aspect of this invention there is provided a composition for conditioning a formed metal surface suitable for use as a beverage can which consists essentially of (a) water; (b) one or more ethoxylated compound(s) selected from ethoxylated phosphate esters, ethoxylated alcohols, ethoxylated fatty acids, ethoxylated hydroxy-substituted fatty acids, and the salts, amides, ethers and esters of ethoxylated fatty acids and of ethoxylated hydroxy-substituted fatty acids; and (c)

- a biocidal material in an amount effective to prevent deterioration of the lubricant and surface-conditioner composition during storage or use; and/or
- an anti-foam agent in sufficient amount to significantly reduce foaming during use.

The lubricant and surface-conditioner composition normally has a pH between 1 and 6.6, preferably between 2.5 and 5. The dissolved organic material may advantageously be any one or more of the following ethoxylates, namely ethoxylated fatty acids, salts of ethoxylated fatty acids, ethoxylated alcohols having at least 4 carbon atoms and containing up to 20 moles of condensed ethylene oxide per mole of alcohol, and ethoxylated alkyl alcohol phosphate esters.

Any antimicrobial or biocidal agent, except those having some detrimental effect on the mobility-enhancing properties or the stability of the compositions, can be employed, as long as it is present in an amount sufficient to effectively inhibit the growth of microorganisms. Hydrogen peroxide is however most preferred for this purpose.

In aqueous concentrated compositions, suitable for dilution with about 99 times their own weight of water to make a composition ready for direct application to metal to enhance mobility after drying, as already described,

concentrations of hydrogen peroxide in the range from 0.375 to 3.75 % are preferred, with concentrations in the range from 1.4 - 2.2% most preferred. In more concentrated compositions the preferred biocide concentrations would be determined by the expected degree of dilution of the concentrate. In general, however, because of the relatively low stability of concentrated hydrogen peroxide, it is preferred that this component, if used, be added only to a sufficiently dilute concentrate that the concentration of hydrogen peroxide does not exceed about 3 wt%. at the time of making up the composition.

Any anti-foam agent, except those which have some detrimental effect on the mobility-enhancing properties already described or the stability of the compositions, may advantageously be added to the compositions as previously taught herein, in an amount effective to decrease the amount of foaming observed during preparation and/or use of the compositions. The preferred anti-foam agent is a combination of wax, low volatility liquid paraffin hydrocarbons, and high molecular weight fatty acid derivatives. Generally, silicone anti-foam agents are not desirable for use with this invention because they tend to cause formation of water breaks. An amount of anti-foam agent corresponding to 0.05 to 2 wt% is generally preferred, with 0.5 to 1 wt% usually more preferred.

According to another aspect of this invention there are also provided processes in which the surface of a previously-formed aluminium article, already de-greased and

cleaned to remove aluminium fines and other solid contamination therefrom and thereafter water-rinsed, is treated by contact while still wet from the water-rinse with a liquid, aqueous multi-component composition as herein disclosed.

By means of this treatment the surface can be effectively and advantageously surface-conditioned so as to impart increased mobility, i.e. a low coefficient of static surface friction, to the surface when subsequently dried, without harming the reflectivity or printability of the thus-treated surface or the adherence of lacquer thereto.

The process of this invention will normally include the preliminary preparation of a degreased, cleaned and still-wet aluminium surface by the steps of:

- (a) cleaning the surface of the aluminium article, already pre-formed to the shape and size intended for final use, by contacting it for an effective time with an aqueous-based liquid cleaning composition so constituted as to produce a thoroughly-degreased, clean surface substantially free from aluminium fines and other solid contamination; and
- (b) rinsing the thus-cleaned surface with additional water, and preferably while still wet therefrom effecting the treatment.

The process of the invention also, almost inevitably, will normally include the subsequent step of drying the treated surface.

The process of the invention is best applied to formed aluminium articles, which will desirably be treated by

contacting them with the multi-component composition at an effective temperature for such a period as to ensure that after drying the treated surface has a coefficient of static surface friction of less than 1.5. Aluminium articles such as cans after they have been treated and dried can then very readily be conveyed, with increased mobility, via high-speed automatic conveying equipment to a lacquering and/or printing station.

The cans may be evaluated for their coefficient of static friction using a laboratory static friction tester. This device measures the static friction associated with the surface characteristics of aluminium cans. This is done by using a ramp which is raised through an arc of 90° by using a constant speed motor, a spool and a cable attached to the free swinging end of the ramp. A cradle attached to the bottom of the ramp is used to hold 2 cans in horizontal position approximately 0.5 inches apart with the domes facing the fixed end of the ramp. A third can is laid upon the 2 cans with the dome facing the free swinging end of the ramp, and the edges of all 3 cans are aligned so that they are even with each other.

As the ramp begins to move through its arc a timer is automatically actuated. When the ramp reaches the angle at which the third can slides freely from the 2 lower cans, a photoelectric switch shuts off the timer. It is this time, recorded in seconds, which is commonly referred to as "slip time". The coefficient of static friction is equal to the

tangent of the angle swept by the ramp at the time the can begins to move.

The compositions and processes of this invention, characterized by the presence of the biocide and/or anti-foaming agent, may be otherwise conventional, eg of the kind typified by the disclosure of our aforesaid U.S. Patent No. 4,859,351, but it is of course advantageous if they are of the improved kind disclosed in our aforesaid co-pending Application No. 9105316.5 of even date herewith. We therefore recommend that the compositions of this invention apart from the biocide(s) and/or anti-foaming agent(s) should incorporate components (A), (B) and (C) as previously identified herein.

In the context of such preferred compositions, it may be noted that not all of the specified components must be separate materials. Fluorozirconic acid (i.e. H_2ZrF_6) can for example serve simultaneously both as component (B) and as component (C).

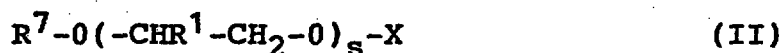
It is also preferable for component (A) to be a compound conforming to general formula I wherein each of x and z is zero, and each of R^2 and R^5 is hydrogen or a cation or cation fraction, and such materials can serve as all of components (A), (B) and (C), for example if R^2 is hydrogen and R^5 is $(1/3)\text{Fe}^{+3}$.

The metal-etching component (C) is preferably one or a

mixture of more than one of the following acidic substances, namely nitric acid, sulfuric acid, phosphoric acid, hydrofluoric acid, hydrochloric acid, hydrobromic acid and hydroiodic acid, as well as acid salts of sulfuric and phosphoric acid, and also salts of nitric, sulfuric, phosphoric, hydrofluoric, hydrochloric, hydrobromic and hydroiodic acids having an ionization product constant less than that of the acid with which they form the salt.

Optionally but preferably, such multi-component compositions also comprise:

-(D) one or more compounds conforming to the general formula:

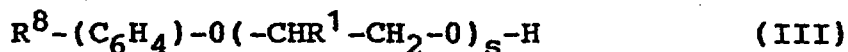


(wherein R^7 is a linear, cyclic or branched saturated monovalent aliphatic hydrocarbon moiety containing from 1 to 25 carbon atoms, X is hydrogen, halogen, phenyl or R^1 , while s is an integer from 1 to 50, and R^1 has the same meaning as in general formula I), the amount of component (D) being sufficient to stabilize the liquid composition against phase-separation.

Preferably component (D) will be one or more of the compounds of general formula (II) wherein R^7 contains from 4 to 20 carbon atoms, and/or s is an integer of from 1 to 20.

Again optionally but preferably, such multi-component compositions also comprise:

-(E) one or more compounds conforming to the general formula:



(wherein R^8 is a linear, cyclic or branched saturated monovalent aliphatic hydrocarbon moiety containing from 4 to 25 carbon atoms, (C_6H_4) is an ortho, meta, or para phenylene nucleus, and R^1 and s have the same meanings as in general formula II above), the amount of component (E) being sufficient to stabilise the liquid composition against phase-separation.

It is also preferred that component (E) should be one or more compounds of general formula (III) wherein R^8 contains from 8 to 12 carbon atoms, and most advantageously 9 carbon atoms.

Optionally but preferably the multi-component composition also comprises:

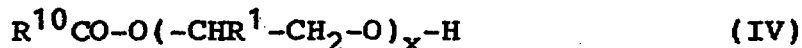
-(F) one or more chelating agents for the metal-containing ions of component (B).

The chelating agents employed can advantageously be compounds (including polymers) the molecular structure of which contains at least two amino, substituted amino, carboxyl, phosphonate, sulfonate and/or carbonyl moieties.

Optionally but preferably the multi-component composition also comprises:

-(G) one or more compounds conforming to the general

formula:



(wherein R^{10} is a linear or branched, saturated or unsaturated monovalent aliphatic hydrocarbon moiety containing from 1 to 25 carbon atoms; and R^1 and x have the same meaning as in general formula (I).

The compound of general formula (IV) will desirably be one containing from 4 to 20 carbon atoms.

It has been found desirable in the process according to the invention to employ as component (A) a compound of general formula I wherein each of R^1 , R^3 and R^6 is hydrogen, each of x and z is zero, and y is not less than about 0.5 times the number of carbon atoms in R^4 .

It has also been found preferable to employ a liquid composition in which:

- (i) the concentration of phosphorus is in the range from about 0.00001 to about 0.0032 gram atoms per litre;
- (ii) the total concentration of all the metal atoms in component (B) is in the range from about 0.00001 to about 0.01 gram atoms per litre;
- (iii) the total concentration of components (A), (B) and (C) is between about 0.005 and about 0.05 % by weight;
- (iv) the pH is between 2 and about 5; and
- (v) the temperature during contact with the aluminium

surface is between 21° and 54°C.

Furthermore it is advantageous if the ratio by weight of component (D) to component (E) is in the range of from 3:1 to 1:3, and the ratio by weight of the combined components (D) and (E) to component (A) is in the range of from 3.3:1 to 1:2.

In the process of this invention it is preferred that the ratio by weight of component (D) to component (E) is in the range of from 1.7:1 to 1:1.4, and the ratio by weight of the combined components (D) and (E) to component (A) is in the range of from 1.8:1 to 1:1.5.

Moreover, it has been found desirable to employ a multi-component composition wherein component (D) is a compound conforming to general formula II wherein R^1 is hydrogen, R^7 contains 4 - 20 carbon atoms, and s is an integer from 1 to 20; and wherein component (E) is a compound conforming to general formula III wherein R^1 is hydrogen, R^8 contains 8 - 12 carbon atoms, and s is an integer from 1 to 20.

Besides the various components (A) to (G) already discussed above the liquid aqueous compositions of this invention also of course contain water. The water used need not necessarily be deionized or otherwise specially purified; ordinary tap water usually gives satisfactory results. The pH of the composition during contact with a

formed aluminium surface should preferably be in the range of 2 - 5. The pH may be adjusted, preferably with nitric and/or sulfuric acid, as necessary during use in order to maintain the pH within the desired range.

The temperature of the composition during contact with the formed aluminium surface is preferably from 10 to 85°C, more desirably from 21 to 54°C.

Contact may be effected by spraying, immersion or any other convenient method, or combination of methods. Preferably the time of contact is from 5 to 60 seconds more preferably 20 to 30 seconds.

It is also generally preferable to rinse the treated surface first with tap water and then again with deionized water after treatment according to the invention and before further processing, such as drying, printing, lacquering or the like.

The processes and compositions used in accordance with this invention display clear advantages over anything herebefore available. Of course, all the advantages of increased mobility, low surface coefficient of friction, high-quality printability, and good adhesion of lacquers and the like, as taught in the aforesaid United States Patent No. 4,859,351, are retained for treatments according to this invention. Specifically, when using the recommended compositions and processes of this invention:

- after treatment according to this invention, a surface can be rinsed with tap or deionized water, without losing its improved surface mobility and other advantages, many more times than a surface treated according to the Examples of the aforesaid United States Patent No. 4,859,351;

- if there is prolonged contact between the treated surface and a cleaning composition or one of the rinses after cleaning but prior to treatment with a composition according to this invention (for example as a result of unplanned stoppages of a high-speed production line), light-to-deep brown spots, believed to be hydrated aluminium oxide, sometimes form on the treated surface; any such spots are removed by treatment according to this invention, whereas they usually persist after using a process as taught in the Examples of the aforesaid United States Patent No. 4,859,351;

- a process according to this invention may more readily be operated at a pH sufficiently low to inhibit bacterial growth than one according to the Examples of the aforesaid United States Patent No. 4,859,351;

- almost any readily-available industrial or tap water supply may be used for make-up or dilution of a composition according to this invention, while the compositions disclosed in the aforesaid United States Patent No. 4,859,351 generally needs deionized water for best results;

and

- the surfaces produced by a process according to the present invention are very readily wetted by water and thus remain free from "water breaks", which are considered undesirable by most aluminium can processors, whereas cans processed according to the Examples of the aforesaid United States Patent No. 4,859,351 are much more likely to exhibit water breaks.

Besides the above-stated advantages of the recommended compositions, which of course are enjoyed equally by those of our aforesaid co-pending Application No. 91-05316.5, it will be appreciated that the multi-component compositions herein disclosed may be operated successfully over quite a wide range of pH values, not all of which will necessarily be inhibitory to bacterial growth because the presence of an effective amount of a biocide advantageously hydrogen peroxide, extends their resistance to biodegradation. Furthermore, the presence of an effective amount of an anti-foaming agent ensures that in the application of the compositions to bring them into contact with the aluminium or other metallic surface there cannot be problems created by foaming.

In order that the invention may be well understood it will now be described in more detail, though only by way of illustration, with reference to the following working

example:

EXAMPLE

Example 1: Surface-conditioner Composition containing
both Biocide and Anti-Foaming Agent

A composition was prepared which is generally-speaking in accordance with the aforesaid United States Patent No. 4,859,351, but which also contains a preferred antifoam agent and a preferred biocide, as follows:

A first concentrate was prepared by first melting 880 parts by weight of ETHOX (registered trade mark) MI-14 (an ethoxylated non-ionic surfactant commercially-available from Ethox Chemicals, Inc., of Greenville, South Carolina, U.S.A.) in a mixing tank at 27 - 32 °C, then mixing in 60 parts by weight of COLLOID 999 (registered trade mark) (a high molecular weight fatty acid derivative, available commercially from Colloids, Inc., 394 Frelinghuysen Ave., Newark, New Jersey 07114, U.S.A.) followed by 60 parts by weight of GP-295TM Defoamer (a suspension of about 10% solid wax in white mineral oil, available commercially from Genese Polymers Corp., Flint, Michigan 48507, U.S.A.). These ingredients mixed to form a cloudy but visually-homogenous liquid with no lumps.

A second concentrate, capable of storage for a period of at least several months, was then made by mixing 47 parts

by weight of the above-described first concentrate with 917 parts by weight of water, preferably deionized water, and with 40 parts by weight of 37.5% aqueous hydrogen peroxide. This second concentrate may then be diluted when desired to make a composition suitable for directly treating aluminium surfaces, in the manner already generally described in United States Patent No. 4,859,351.



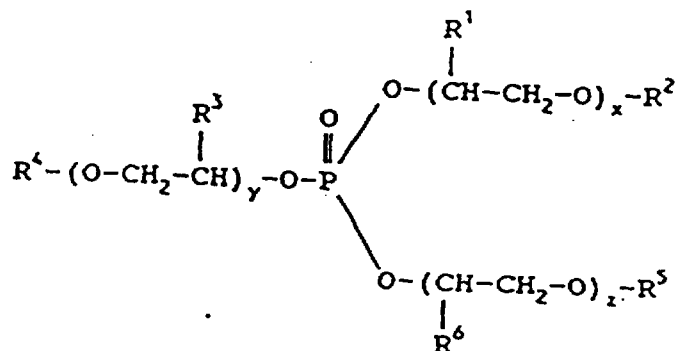
CLAIMS

1. A composition for conditioning a formed metal surface suitable for use as a beverage can which composition consists essentially of (a) water; (b) one or more ethoxylated compound(s) selected from ethoxylated phosphate esters, ethoxylated alcohols, ethoxylated fatty acids, ethoxylated hydroxy-substituted fatty acids, and the salts, amides, ethers and esters of ethoxylated fatty acids and of ethoxylated hydroxy-substituted fatty acids; and (c)

- a biocidal material in an amount effective to prevent deterioration of the lubricant and surface-conditioner composition during storage or use; and/or

- an anti-foam agent in an amount sufficient significantly to reduce foaming during use; and, optionally, one or more compounds selected from (A) to (G):

-(A) one or more water-soluble materials conforming to the general formula:



(I)



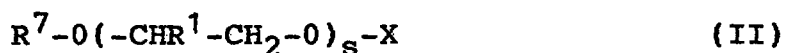
- 20 -

(wherein each of R^1 , R^3 and R^6 , which may be the same or different, is hydrogen or an alkyl group containing from 1 to 4 carbon atoms, each of x , y and z is zero or an integer from 1 to 25, and each of R^2 , R^4 and R^5 , which may be the same or different, is hydrogen or a monovalent cation or a monovalent fraction of a polyvalent cation or an alkyl, aryl or arylalkyl group containing from 1 to 20 carbon atoms, provided however that at least one of R^2 , R^4 and R^5 (i) is not hydrogen and (ii) has at least one alkoxy group interposed between it and the phosphorus atom);

-(B) one or more water-soluble salts containing ions that include one or more Fe, Zr, Sn, Al and/or Ce atom(s);

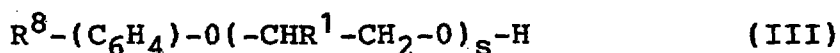
-(C) one or more water-soluble metal-etching compounds;

-(D) one or more compounds conforming to the general formula:



(wherein R^7 is a linear, cyclic or branched saturated monovalent aliphatic hydrocarbon moiety containing from 1 to 25 carbon atoms, X is hydrogen, halogen, phenyl or R^1 , while s is an integer from 1 to 50, and R^1 has the same meaning as in general formula I);

-(E) one or more compounds conforming to the general formula:



(wherein R^8 is a linear, cyclic or branched saturated monovalent aliphatic hydrocarbon moiety containing from 4 to



25 carbon atoms, (C_6H_4) is an ortho, meta, or para phenylene nucleus, and R^1 and s have the same meanings as in general formula II above); and

-(F) one or more chelating agents for the metal-containing ions of component (B)

whereby, once dried, the mobility of the formed metal surface is enhanced whilst substantially maintaining its reflectivity and ability to adhere paint, ink, lacquer or the like.

2. A composition as claimed in claim 1, in which the anti-foam agent, when present, is in a concentration in the range of from 0.05 to 2 wt.%

3. A composition as claimed in claim 2, in which the anti-foam agent, when present, is in a concentration in the range of from 0.5 to 1 wt.%.

4. A composition as claimed in any preceding claim, which has a pH value of between 1 and 6.6.

5. A composition as claimed in any preceding claim, which has a pH value of between 2.5 and 5.

6. A composition as claimed in any of the preceding claims, in which the ethoxylated compound is or includes one or more ethoxylated fatty acid(s), salt(s) of such ethoxylated fatty acid(s), alcohol(s) having at least 4 carbon atoms and ethoxylated with up to 20 moles of condensed ethylene oxide per mole of such alcohol(s), and/or ethoxylated alkyl alcohol phosphate ester(s).



7. A composition as claimed in any of the preceding claims, in which the biocide, when present, is or includes hydrogen peroxide.

8. A composition as claimed in claim 7, which contains hydrogen peroxide in a concentration within the range of from 0.375 to 3.75%.

9. A composition as claimed in claim 7, in which the concentration of hydrogen peroxide does not exceed 3 wt.%.

10. A composition as claimed in any of claims 7 to 9, which contains hydrogen peroxide in a concentration within the range of from 1.4 to 2.2%.

11. A composition as claimed in any of the preceding claims, in which the anti-foam agent, when present, is or includes a combination of wax, low-volatility liquid paraffin hydrocarbon(s) and high molecular weight fatty acid derivative(s).

12. A composition as claimed in any of the preceding claims and substantially as herein described with reference to the Example.

13. A process for surface-conditioning and imparting increased mobility to the surface of a previously-formed metal article, in which said surface already de-greased and cleaned to remove metal fines and other solid contamination therefrom and thereafter water-rinsed, is treated by contact while still wet from the water-rinse with a composition comprising (a) water; (b) one or more ethoxylated



compound(s) selected from ethoxylated phosphate esters, ethoxylated alcohols, ethoxylated fatty acids, ethoxylated hydroxy-substituted fatty acids, and the salts, amides, ethers and esters of ethoxylated fatty acids and of ethoxylated hydroxy-substituted fatty acids; and (c)

- a biocidal material in an amount effective to prevent deterioration of the lubricant and surface-conditioner composition during storage or use; and/or

- an anti-foam agent in an amount sufficient significantly to reduce foaming during use,

whereby, once dried, the mobility of the formed metal surface is enhanced whilst substantially maintaining its reflectivity and ability to adhere paint, ink, lacquer or the like.

14. A process as claimed in claim 13, wherein the metal is aluminium.

15. A process as claimed in claim 14, which includes the preliminary preparation of a degreased, cleaned and still-wet aluminium surface by the steps of:

(a) cleaning the surface of the aluminium article, already pre-formed to the shape and size intended for final use, by contacting it for an effective time with an aqueous-based liquid cleaning composition so constituted as to produce a thoroughly-degreased, clean surface substantially free from aluminium fines and other solid contaminants; and

(b) rinsing the thus-cleaned surface with additional



water, and while still wet therefrom effecting the treatment.

16. A process as claimed in claim 14 or claim 15, which includes the subsequent step of drying the treated surface.

17. A process as claimed in any of claims 14 to 16, in which the pre-formed aluminium articles are treated by contacting them with the composition at an effective temperature for such a period as to ensure that after drying the treated surface has a coefficient of static friction of less than 1.5.

18. A process as claimed in any of claims 13 to 17, in which during the treatment the composition is adjusted to and maintained at a pH within the range of from 2 to 5.

19. A process as claimed in any of claims 13 to 18, in which the treatment with the composition is conducted at a temperature in the range of from 10 to 85°C.

20. A process as claimed in claim 19, in which the treatment is conducted at a temperature in the range of from 21° to 54°C.

21. A process as claimed in any of claims 13 to 20, in which the treatment is effected by contacting the surface with the composition for a contact-period of from 5 to 60 seconds.

22. A process as claimed in claim 21, in which the contact-period is from 20 to 30 seconds.



- 25 -

23. A process as claimed in any of claims 13 to 22, in which the thus-treated surface before drying is rinsed first with tap water and then again with de-ionized water.
