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(54) **Process for treating formed metal surfaces**

(57) A process for treating an aluminium can, comprising the steps of cleaning with an aqueous acidic or alkaline solution, drying and subsequently conveying the cleaned and dried can via automatic conveying equipment to a location where it is lacquered or decorated by printing or both. At least one exterior surface of the can, prior to the last drying of the surface before automatic conveying, is contacted with a lubricant and surface conditioner forming composition comprising ethoxylated, hydrogenated castor oil triglycerides, and the can is then dried without subsequent rinsing, thereby forming a film on the can to provide the surface of the can after drying with a reduced coefficient of static friction compared to an otherwise identical sequence of treatments where the lubricant and surface conditioner forming composition is substituted with water.

EP 0 969 078 A2

Description

[0001] This Application is divided from European Patent Application No. 93 9 16982.7.

[0002] This invention relates to processes and compositions which accomplish at least one, and most preferably all, of the following related objectives when applied to formed metal surfaces, more particularly to the surfaces of cleaned aluminum and/or tin plated cans: (i) reducing the coefficient of static friction of the treated surfaces after drying of such surfaces, without adversely affecting the adhesion of paints or lacquers applied thereto; (ii) promoting the drainage of water from treated surfaces, without causing "water-breaks", i.e., promoting drainage that results in a thin, continuous film of water on the cans, instead of distinct water droplets separated by the relatively dry areas called "water-breaks" between the water droplets; and (iii) lowering the dryoff oven temperature required for drying said surfaces after they have been rinsed with water.

[0003] The following discussion and the description of the invention will be set forth primarily for aluminum cans, as these represent the largest volume area of application of the invention. However, it is to be understood that, with the obviously necessary modifications, both the discussion and the description of the invention apply also to tin plated steel cans and to other types of formed metal surfaces for which any of the above stated intended purposes of the invention is practically interesting.

[0004] Aluminum cans are commonly used as containers for a wide variety of products. After their manufacture, the aluminum cans are typically washed with acidic cleaners to remove aluminum fines and other contaminants therefrom. Environmental considerations and the possibility that residues remaining on the cans following acidic cleaning could influence the flavor of beverages packaged in the cans has led to an interest in alkaline or acid cleaning to remove such fines and contaminants. However, such cleaning of aluminum cans generally results in differential rates of metal surface etch on the outside versus on the inside of the cans. For example, optimum conditions required to attain an aluminum fine-free surface on the inside of the cans usually leads to can mobility problems on conveyors because of the increased roughness on the outside can surface.

[0005] Aluminum cans that lack a low coefficient of static friction (hereinafter often abbreviated as "COF") on the outside surface usually do not move past each other and through the trackwork of a can plant smoothly. Clearing the jams resulting from failures of smooth flow is inconvenient to the persons operating the plant and costly because of lost production. The COF of the internal surface is also important when the cans are processed through most conventional can decorators. The operation of these machines requires cans to slide onto a rotating mandrel which is then used to transfer the can past rotating cylinders which transfer decorative inks to the exterior surface of the cans. A can that does not slide easily on or off the mandrel can not be decorated properly and results in a production fault called a "printer trip". In addition to the misloaded can that directly causes such a printer trip, three to four cans before and after the misloaded one are generally lost as a consequence of the mechanics of the printer and conveyor systems. Jams and printer trips have become increasingly troublesome problems as line speed have increased during recent years to levels of about 1200 to 1500 cans per minute that are now common. Thus, a need has arisen in the can manufacturing industry, particularly with aluminum cans, to modify the COF on the outside and inside surfaces of the cans to improve their mobility.

[0006] An important consideration in modifying the surface properties of cans is the concern that such modification may interfere with or adversely affect the ability of the can to be printed when passed to a printing or labeling station. For example, after cleaning the cans, labels may be printed on their outside surface, and lacquers may be sprayed on their inside surface. In such a case, the adhesion of the paints and lacquers is of major concern. It is therefore an object of this invention to improve mobility without adversely affecting adhesion of paints, decorating inks, lacquers, or the like.

[0007] In addition, the current trend in the can manufacturing industry is directed toward using thinner gauges of aluminum metal stock. The down-gauging of aluminum can metal stock has caused a production problem in that, after washing, the cans require a lower drying oven temperature in order to pass the column strength pressure quality control test. However, lowering the drying oven temperature resulted in the cans not being dry enough when they reached the printing station, and caused label ink smears and a higher rate of can rejects.

[0008] One means of lowering the drying oven temperature would be to reduce the amount of water remaining on the surface of the cans after water rinsing. Thus, it is advantageous to promote the drainage of rinse water from the treated can surfaces. However, in doing so, it is generally important to prevent the formation of surfaces with water-breaks as noted above. Such water-breaks give rise to at least a perception, and increase the possibility in reality, of non-uniformity in practically important properties among various areas of the surfaces treated.

[0009] Thus, it is desirable to provide a means of improving the mobility of aluminum cans through single filers and printers to increase production, reduce line jammings, minimize down time, reduce can spoilage, improve or at least not adversely affect ink laydown, and enable lowering the drying oven temperature of washed cans.

[0010] In the most widely used current commercial practice, at least for large scale operations, aluminum cans are typically subjected to a succession of six cleaning and rinsing operations as described in Table 1 below. (Contact with ambient temperature tap water before any of the stages in Table 1 is sometimes used also; when used, this stage is often called a "vestibule" to the numbered stages.)

Table 1

STAGE NUMBER	ACTION ON SURFACE DURING STAGE
1	Aqueous Acid Precleaning
2	Aqueous Acid and Surfactant Cleaning
3	Tap Water Rinse
4	Mild Acid Postcleaning, Conversion Coating, or Tap Water Rinse
5	Tap Water Rinse
6	Deionized ("DI") Water Rinse

[0011] It is currently possible to produce a can which is satisfactorily mobile and to which subsequently applied inks and/or lacquers have adequate adhesion by using suitable surfactants either in Stage 4 or Stage 6 as noted above. Preferred treatments for use in Stage 6 are described in U. S. Patents 4,944,889 and 4,859,351, and some of them are commercially available from the Parker+Amchem Division of Henkel Corporation (hereinafter often abbreviated as "P+A") under the name ME-40®.

[0012] However, many manufacturers have been found to be reluctant to use chemicals such as ME-40® in Stage 6. In some cases, this reluctance is due to the presence of a carbon filter for the DI water (normal Stage 6) system, a filter that can become inadequately effective as a result of adsorption of lubricant and surface conditioner forming additives such as those in ME-40®; in other cases, it is due to a reluctance to make the engineering changes necessary to run ME-40.

[0013] For those manufacturers that prefer not to add any lubricant and surface conditioner material to the final stage of rinsing but still wish to achieve the advantages that can be obtained by such additions, alternative treatments for use in Stage 4 as described above have been developed and are described in U. S. Patents 5,030,323 and 5,064,500. Some of these materials are commercially available from P+A under the name FIXODINE® 500.

[0014] However, the reduction in coefficient of friction provided by prior art treatments in either Stage 4 or Stage 6 can be substantially reduced, often to an unacceptable level, if the treated cans are subjected to extraordinary heating after completion of the six process stages described above. Such extraordinary heating of the cans in the drying oven occurs whenever a high speed production line is stalled for even a few minutes, an event that is by no means rare in practice. In practical terms, the higher COF measurements correlate with the loss of mobility, thereby defeating the purpose of introducing mobility enhancing surfactants into can washing formulations. Accordingly, it is an object of this invention to provide means of improving the mobility of aluminum cans and/or one of the other objects stated above that are superior to means taught in the prior art, particularly with respect to stability of the beneficial effects to heating well beyond the minimum extent necessary for drying the treated surfaces.

[0015] Other than in the operating examples, or where otherwise indicated, all numbers expressing quantities of ingredients or reaction conditions used herein are to be understood as modified in all instances by the term "about" in describing the broadest scope of the invention. Practice within the numerical limits given, however, is generally preferred.

[0016] Also, unless there is an explicit statement to the contrary, the description below of groups of chemical materials as suitable or preferred for a particular ingredient according to the invention implies that mixtures of two or more of the individual group members are equally as suitable or preferred as the individual members of the group used alone. Furthermore, the specification of chemical materials in ionic form should be understood as implying the presence of some counterions as necessary for electrical neutrality of the total composition. In general, such counterions should first be selected to the extent possible from the ionic materials specified as part of the invention; any remaining counterions needed may generally be selected freely, except for avoiding any counterions that are detrimental to the objects of the invention.

[0017] In accordance with this invention, there is provided a process comprising the steps of cleaning an aluminum can with an aqueous acidic or alkaline cleaning solution, drying the cleaned can, and subsequently conveying the cleaned and dried can *via* automatic conveying equipment to a location where it is lacquered or decorated by printing or both, characterized by contacting at least one exterior surface of said aluminum can, prior to the last drying of said exterior surface before automatic conveying, with a lubricant and surface conditioner forming composition comprising ethoxylated, hydrogenated castor oil triglycerides, and drying the can without subsequent rinsing, thereby forming a film on the can surface to provide the surface of the can after drying with a coefficient of static friction that is not more than 1.5, preferably not more than 1.2, more preferably not more than 1.0, still more preferably not more than 0.80, and is less than the COF that would be obtained by an otherwise identical sequence of treatments except that the lubricant and surface conditioner forming composition is substituted with water only, characterized in that the lubricant and surface conditioner forming composition is an aqueous solution comprising at least one of alkoxylated and non-alkoxylated castor oil triglycerides and hydrogenated castor oil derivatives and at least 0.29 g/l fluozirconic acid. Preferably, the lubricant and surface conditioner forming composition comprises ethoxylated, hydrogenated caster oil triglycerides.

[0018] Preferred alkoxylated, especially ethoxylated, castor oil triglycerides that are commercially available include Trylox® 5900, Trylox® 5902, Trylox® 5904, Trylox® 5906, Trylox® 5907, Trylox® 5909, Trylox® 5918, and preferred hydrogenated castor oil derivatives include commercial materials such as Trylox® 5921 and Trylox® 5922, all available from Henkel Corporation. These materials are particularly useful as additives to final stage rinses, because they provide a dried lubricant and surface conditioner film on the treated surface that resists rise of the COF with heating beyond the minimum necessary to dry the surface.

[0019] Additional improvements can often be achieved, particularly for lubricant and surface condition treatments applied before the final contact of the treated surface with an aqueous composition, by using an inorganic material selected from metallic or ionic zirconium, titanium, cerium, aluminum, iron, vanadium, tantalum, niobium, molybdenum, tungsten, hafnium or tin to produce a film combining one or more of these metals with one or more of the above-described organic materials. A thin film is produced having a coefficient of static friction that is not more than 1.5, preferably not more than 1.2, more preferably not more than 1.0, or still more preferably not more than 0.80, and is less than the coefficient without such film, thereby improving can mobility in high speed conveying without interfering with subsequent lacquering, other painting, printing, or other similar decorating of the containers.

[0020] The technique of incorporating such inorganic materials is described, in particular detail with reference to zirconium containing materials, in U.S. Patents 5,030,323 of July 9, 1991 and 5,064,500 of November 12, 1991. The substitution of other metallic materials for those taught explicitly in one of these patents is within the scope of those skilled in the art.

[0021] In a further preferred embodiment of the process of the present invention, in order to provide improved water solubility, especially for the non-ethoxylated organic materials described herein, and to produce a suitable film on the can surface having a coefficient of static friction no more than 1.5 after drying, one employs a mixture of one or more surfactants, preferably alkoxylated and most preferably ethoxylated, along with such non-ethoxylated organic material to contact the cleaned can surface prior to final drying and conveying. Preferred surfactants include ethoxylated and non-ethoxylated sulfated or sulfonated fatty alcohols, such as lauryl and coco alcohols. Suitable are a wide class of anionic, non-anionic, cationic, or amphoteric surfactants. Alkyl polyglycosides such as C_8 - C_{18} alkyl polyglycosides having average degrees of polymerization between 1.2 and 2.0 are also suitable. Other classes of surfactants suitable in combination are ethoxylated nonyl and octyl phenols containing from 1.5 to 100 moles of ethylene oxide, preferably a nonylphenol condensed with from 6 to 50 moles of ethylene oxide such as Igepal® CO-887 available from Rhone-Poulenc; alkyl/aryl polyethers, for example, Triton® DF-16; and phosphate esters of which Triton® H-66 and Triton® QS-44 are examples, all of the Triton® products being available from Union Carbide Co., and Ethox® 2684 and Ethfac® 136, both available from Ethox Chemicals Inc., are representative examples; polyethoxylated and/or polypropoxylated derivatives of linear and branched alcohols and derivatives thereof, as for example Trycol® 6720 (Henkel Corp.), Surfonic® LF-17 (Texaco) and Antarox® LF-330 (Rhone-Poulenc); sulfonated derivatives of linear or branched aliphatic alcohols, for example, Neodol® 25-3S (Shell Chemical Co.); sulfonated aryl derivatives, for example, Dyasulf® 9268-A, Dyasulf® C-70, Lomar® D (all available from Henkel Corp.) and Dowfax® 2A1 (available from Dow Chemical Co.); and ethylene oxide and propylene oxide copolymers, for example, Pluronic® L-6 1, Pluronic® 81, Pluronic® 31R1, Tetronic® 701, Tetronic® 90R4 and Tetronic® 150R1, all available from BASF Corp.

[0022] Further, the lubricant and surface conditioner n accordance with this invention may comprise a phosphate acid ester or preferably an ethoxylated alkyl alcohol phosphate ester. Such phosphate esters are commercially available under the trade name Gafac® PE 510 from GAF Corporation, Wayne, NJ, and as Ethfac® 136 and Ethfac® 161 from Ethox Chemicals, Inc., Greenville, SC. In general, the organic phosphate esters may comprise alkyl and aryl phosphate esters with and without ethoxylation.

[0023] The lubricant and surface conditioner for aluminum cans may be applied to the cans during their wash cycle, during one of their treatment cycles such as cleaning or conversion coating, during one of their water rinse cycles, or during their final water rinse cycle. In addition, the lubricant and surface conditioner may be applied to the cans after their final water rinse cycle, i.e., prior to oven drying, or after oven drying, by fine mist application from water or another volatile non-inflammable solvent solution. It has been found that the lubricant and surface conditioner is capable of depositing on the surface to provide it with the desired characteristics. The lubricant and surface conditioner may be applied by spraying and interacts with the surface through chemisorption or physiosorption to provide it with the desired dried lubricant and surface conditioner film.

[0024] The amount of lubricant and surface conditioner to be applied to the cans should be sufficient to reduce the coefficient of static friction on the outside surface of the cans to a value of about 1.5 or lower, and preferably to a value of about 1 or lower. Generally speaking, such amount should be on the order of from about 3 mg/m^2 to about 60 mg/m^2

of lubricant and surface conditioner on the outside surface of the cans.

[0025] For a fuller appreciation of the invention, reference should be made to the following examples, which are intended to be merely descriptive, illustrative, and not limiting as to the scope of the invention.

Examples Group I

[0026] Uncleaned aluminum cans from an industrial can manufacturer are washed clean in examples Type A with alkaline cleaner available from Parker+Amchem Division, Henkel Corporation, Madison Heights, Michigan, employing the Ridoline® 3060/306 process and in Examples Type B with an acidic cleaner, Ridoline® 125 CO from the same company. Following initial rinsing and before final drying, the cleaned cans are treated with a lubricant and surface conditioner composition comprising one of the following (i) about a 1 % by weight aqueous solution in deionized water of active organic material (I) as specified in Table 2 below; (ii) about 1 % of the active organic (I) in deionized water plus about 2 gm/l (0.2 %) of the inorganic constituent (II) as specified in Table 2; (iii) about 1% active organic (I) in deionized water plus about 0.5 % of surfactant (III) as specified in Table 2; (iv) about 1 % active organic (I), about 0.2% inorganic (II), and about 0.5% surfactant (III) as specified in Table 2.

[0027] Among the compositions of the aqueous lubrication and surface conditioning treatment in this group, the ones containing inorganic constituent (II) from Table 2 are applied in Stage 4 as defined above, while those not containing this ingredient are applied immediately before final drying.

[0028] In addition, the cans after drying are evaluated for their coefficient of static friction using a custom built slip time tester. This apparatus consisted of three timing stations attached to a motor driven inclinable ramp. Two cans are placed horizontally in each station and a third placed on top of them in the opposite direction. This procedure insures that the burr on the cut edge of the cans does not interfere with the motion of the cans. The test begins as the ramp is raised toward the vertical. The elapsed time from the start of the ramps movement to the time when the third can slides is recorded as the "Slip Time". This time is then converted into a (Static) Coefficient of Friction ("COF") according to the equation:

$$\text{COF} = \text{Tangent of } [4.84 + (2.79 \cdot t)]$$

where t is the time Slip Time in seconds. Fifteen slip times were collected, converted to COF's and then averaged to give the COF result discussed here. In some cases the tested cans were subjected to an additional bake out at 210° C for 5 minutes and the COF redetermined; this result is denoted hereinafter as "**COF-2**".

[0029] In all cases in this group of examples, the COF produced on the surface is less than 1.5.

Examples and Comparison Examples Group III

[0030] The combination of ethoxylated castor oil derivatives and fluozironic acid shown in Table 2 above has been found to have an unexpected additional advantage, which is illustrated further in this group.

[0031] Some beverages packaged in aluminum cans are pasteurized, and unless the temperature and composition(s) of the aqueous solution(s) with which cans are contacted during pasteurization are very carefully controlled, staining of the dome of the can often occurs during pasteurization. A final rinse mobility enhancer (FRME) combining fluozirconic acid and hydrogenated ethoxylated castor oil derivatives in proper concentrations has been found to provide both protection against dome staining during pasteurization and adequate lowering of the COF for most purposes.

[0032] The can washing setup for this group of examples was:

Stage 1	sulfuric acid, pH 2.0, 30 sec., 54.4° C
Stage 2	RIDOLINE® 124C, 15 mL Free Acid, 3.4 g/L total of surfactant, Fluoride Activity - 10 mV, 90 sec., 54.4° C
Stage 3	deionized water, 150 sec. (ca. 17.7 L)
Stage 4	as noted in Table 7 and below, 20 sec. spray + 20 sec. dwell, 29.4° C temperature
Stage 5	not used
Stage 6	not used

[0033] In addition to the ingredients listed in Table 7, the solutions were all adjusted to pH 4.5 by addition of aqueous ammonia or nitric acid as required.

[0034] Dome staining was evaluated by first removing the domes from the treated cans with a can opener. The domes were then placed in a water bath containing 0.2 g/L of borax at 65.6° C for 30 minutes, then rinsed in deionized water and dried in an oven. Staining resistance was evaluated visually by comparison with known satisfactory and unsatisfactory standards. Results are shown in Table 7. The last two conditions shown in the Table are highly satisfactory with respect to both COF and dome staining resistance during pasteurization.

Table 7

EFFECT OF CONCENTRATIONS OF ETHOXYLATED CASTOR OIL DERIVATIVE AND OF FLUOZIRCONIC ACID ON DOME STAINING RESISTANCE AND COEFFICIENT OF FRICTION			
Grams of H_2ZrF_6/Liter	Grams of Trylox™ 5921/Liter	COF	Pasteurization Protection Rating
0	0	1.16	Fail
0	0.2	0.57	Fail
0.14	0.2	0.52	Fail
0.29	0.2	0.61	Marginal
0.58	0.2	0.63	Pass
1.16	0.2	0.70	Pass

Claims

1. A process comprising the steps of cleaning an aluminum can with an aqueous acidic or alkaline cleaning solution, drying the cleaned can, and subsequently conveying the cleaned and dried can *via* automatic conveying equipment to a location where it is lacquered or decorated by printing or both, characterized by contacting at least one exterior surface of said aluminum can, prior to the last drying of said exterior surface before automatic conveying, with a lubricant and surface conditioner forming composition comprising ethoxylated, hydrogenated castor oil triglycerides, and drying the can without subsequent rinsing, thereby forming a film on the can surface to provide the surface of the can after drying with a coefficient of static friction that is not more than 1.5, preferably not more than 1.2, more preferably not more than 1.0, and still more preferably not more than 0.80, and is less than the COF that would be obtained by an otherwise identical sequence of treatments except that the lubricant and surface conditioner forming composition is substituted with water only, characterized in that the lubricant and surface conditioner forming composition is an aqueous solution comprising at least one of alkoxylated and non-alkoxylated castor oil triglycerides and hydrogenated castor oil derivatives and at least 0.29 g/l of fluozirconic acid.