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PROCESS FOR DRYING METAL ARTICLES

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This invention relates to the drying of articles of metal and other non-absorbent materials and more particularly to the removal of contaminating aqueous liquid from such articles by means of volatile organic liquids.

In processes involving electro-deposition of metals on numerous metallic articles it is necessary on removing the articles from the electrolyte to cleanse them of all adhering salts. This is done generally by washing the articles with water or an aqueous solution and usually by immersing them in water tanks. After water washing, the articles are thoroughly dried. Frequently this is effected by exposing them to heat, conveniently in a stream of hot air. However, as the water evaporates away it gathers into droplets and eventually there appear at the places from which the droplets of water were finally dried off spots or stains which can only be removed by the tedious and expensive method of hand wiping and which in some cases cannot be satisfactorily removed even by that means. Particularly this is the case with bright electroplated articles such as jewelry, bezels and other parts of watches, cosmetic containers, instrument parts and the like. Sometimes the drying process is speeded up by immersing the washed articles in a chlorinated solvent such as trichloroethylene or perchloroethylene in the form of liquid or vapour. While this may rapidly remove the bulk of the water, it does not remove it completely and there still remain numerous small droplets which eventually produce water stains that can only be removed by hand wiping.

Another method that is widely used for drying water-wet articles is tumbling in barrels of sawdust. This is effective, but slow, and it is inconvenient for treating large articles. Its main disadvantage, however, is the difficulty of eventually separating the treated articles from the sawdust. Either the articles must be picked out by hand or the whole content of the barrel must be sieved and in either case intricately shaped articles will retain particles of sawdust which lodge in relatively inaccessible places and are difficult to remove. Even simply shaped articles are liable to retain an adhering film of very fine dust which must be subsequently removed by the tedious process of hand wiping.

Again the problems of drying metal surfaces quickly and efficiently without leaving stains or salt deposits thereon arise in an acute form when metal articles are subjected to aqueous cleansing and preparative processes prior to painting, enamelling, lacquering or varnishing; such preparative processes may be, for instance, chemical treatments such as acid pickling, alkaline derusting, phosphating or chromating. Other processes of surface preparation, for instance, contour etching, electroplating anodising and electroplating are likewise carried out in aqueous baths the liquors from which must finally be washed from the treated surfaces, which then must be rinsed and dried.

In these and other fields the requirements are now so exacting and the preparation of the surfaces has reached such perfection that unless the final rinsing of the surface is carried out with liberal quantities of deionised water, the result may be unsatisfactory. If less pure water is used, then even if the rinsing is followed by a treatment with a solvent such as trichloroethylene, some water droplets eventually remain on the surface and as

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these are dried off by heat there are produced local concentrations of residual salts; these will mar the perfection of a bright metal finish or may cause serious blistering if the prepared surface after subsequent painting, enamelling, lacquering or varnishing comes to be stored in humid or hot and humid conditions.

We have now found that the aforementioned difficulties may be overcome and an improved result obtained if the wet articles of metal or other non-absorbent material are first brought into contact with a chlorinated hydrocarbon solvent such as trichloroethylene, perchloroethylene, methylene chloride or carbon tetrachloride containing dissolved therein a small proportion of a cationic surface active agent. By this means the adhering water is completely removed by the chlorinated solvent and no further drying is necessary; the residual solvent is itself readily removed by gentle heat or by means of a stream of gas.

The invention therefore provides a process for drying water-contaminated surfaces of articles of metal or other non-absorbent material which comprises treating the said surfaces with a chlorinated hydrocarbon solvent containing dissolved therein a small proportion of a cationic surface active agent.

It has already been proposed to dry rigid articles moist with water, particularly metal articles, by immersing them in a water-free boiling solution of a small quantity of a mersolate in a chlorinated hydrocarbon and allowing the articles to remain in the boiling solution until the water has been removed therefrom and expelled from the solution by azeotropic distillation. Mersolates are sodium salts of hydrolysed paraffin wax sulphochlorides and thus are anionic surface active agents. Our process therefore differs radically from this known process in that we utilise instead cationic surface active agents and thereby gain the very considerable technical advantage that, as will be more fully explained hereinafter, we avoid the need for any prolonged azeotropic distillation. The water is quite rapidly displaced from the surface of the article by the solvent and it is not necessary to continue the treatment until the water has been distilled out of the bath. Consequently, it is not necessary for our solvent bath to be water-free. Indeed in its simplest form, which is quite widely applicable, our process consists merely in immersing the moist articles to be treated in the solvent bath, which need not be water-free and which in many cases can even be at room temperature, leaving them for a matter of seconds or at most a few minutes to allow time for the water to be displaced, removing them, draining off surplus solvent and finally drying off the small amount of solvent remaining on the surface by means of gentle heat or a stream of gas. So successful is the displacement of the water by the solvent that we have in many cases observed the remarkable result that the process is effective even if the solvent bath or the articles to be dried are so contaminated with water that a layer of water forms on the surface of the bath, so that on removal therefrom the articles actually pass through a layer of water. Moreover the process can be very conveniently applied following preparative treatments in aqueous baths in which the "Serscal" process for fume prevention has been utilised. This is a procedure wherein fuming and steaming of the bath, (for instance, a phosphating, acid pickling or alkaline cleaning and derusting bath) is controlled by sealing the surface of the bath with a layer of inert material as described in copending applications Nos. 29265/56, 3252/57 and 3258/57. The surface of material drawn from such a bath is wet with water and may also bear traces of oil substances; both aqueous and oily phases are rapidly and completely displaced when brought

into contact with the solution of the cationic surface active agent.

Advantageously, if the highest perfection of a bright finished surface is to be retained with metal articles such as jewelry, watch parts, instrument parts and the like, the articles are first immersed in the chlorinated hydrocarbon solvent containing the cationic surface active agent and after removal are brought into contact with a further quantity of the solvent in the form of liquid or vapour to prevent the formation of the very slight deposit that might otherwise be caused by traces of residual cationic surface active agent. Finally the articles are exposed in the air and as the adhering solvent evaporates it leaves the metal objects bright and free from water and water stains.

For most applications the treatment with the solvent containing the cationic surface active agent may be carried out hot or cold and the liquid may be applied to the article by dipping, spraying or brushing.

For the treatment of small parts the operation is most conveniently carried out in equipment very similar to a standard two-dip degreasing plant. This is an open tank the lower part of which is divided into two compartments each provided with heating means. In the upper part of the tank is a condensing surface which conveniently consists of a coiled tube disposed adjacent to the walls of the tank. Pipework connects the lower portions of the two compartments with each other and with a collecting trough lying immediately below the condensing coil. In normal use, the two compartments each contain the solvent, for instance, trichloroethylene, which is kept boiling and the vapour which rises therefrom is condensed on the coil, the condensed liquid being returned to the base of one or other compartment as desired. When such a plant is used for the purposes of the present invention a simple water settling vessel is preferably interpolated between the collecting trough and the return to the base of the tank. When in use, one of the compartments contains simply a chlorinated hydrocarbon solvent such as trichloroethylene or perchloroethylene and the other a quantity of the same solvent containing dissolved therein a small proportion of a cationic surface active agent. The solvent in both compartments is kept boiling. The vapour is condensed on the coil and the condensed liquid passes through the water separator and is returned to the first compartment. This is therefore constantly supplied with distilled solvent and is arranged so that it overflows into the second compartment which contains the solution of the cationic surface active agent. The articles to be treated are simply immersed for a short time in the latter compartment, are lifted up and allowed to drain, immersed in the distilled solvent in the first compartment, again drained, removed and allowed to dry.

The invention is not, however, limited to the treatment of small objects and indeed it has been found particularly useful for drying large metal panels which have been chemically pretreated, as for instance, in a phosphating bath, and must then be dried before enamelling, for instance, panels for refrigerators, sink units, or other kitchen equipment. In some circumstances it is convenient to treat such articles at relatively low temperatures, the solvent being perhaps warm but not boiling. The solution of a cationic surface active agent in a chlorinated hydrocarbon solvent is applied by brushing or spraying, the liquid then being collected, the water separated off and the solution returned for re-use; the treated panels are then gently heated to evaporate off residual solvent and are then ready for painting or enamelling.

As suitable chlorinated hydrocarbon solvents for use in our process those customarily used in metal degreasing operations may be employed, for instance, methylene chloride, carbon tetrachloride, trichloroethylene, and perchloroethylene, the last two being much preferred be-

cause they combine a low toxicity with suitable physical properties, for instance, convenient boiling points.

As suitable cationic surface active agents there may be mentioned, for instance, long chain alkyl trimethyl ammonium or pyridium chlorides or bromides such as cetyl pyridium bromide or cetyl trimethyl ammonium bromide, long chain dialkyl dimethyl ammonium chlorides or bromides, for instance, dicetyl dimethyl ammonium bromide and long chain alkyl dimethyl benzyl ammonium chlorides such as cetyl dimethyl benzyl ammonium chloride. These compounds are all quarternary ammonium salts bearing a long chain alkyl substituent and these are in general the preferred classes of agents; however, other types of cationic surface active agents may also be used, for instance, an agent made by condensation of methyl octadecylamine with 4.6 molecular proportions of ethylene oxide.

Surprisingly small quantities of these agents are effective. For instance, we have observed some useful effect with a concentration in the treatment bath as low as 0.001%. On the other hand, if the quantity is too large then there may be an undesirable tendency for the water to be emulsified in the solvent; this effect becomes noticeable in some cases if the concentration of the surface active agent much exceeds about 1%. We prefer, in fact, to work with concentrations in the range 0.1% to 0.3% but greater or smaller concentrations may be used if desired. Usually there seems to be no advantage in increasing the proportion beyond about 0.5%.

As already indicated the process may be worked cold or at any temperature up to the boiling point of the solvent used. The best conditions for any given case are readily determined by a few simple experiments. The time needed for the treatment is surprisingly short and may be anything from a few seconds up to a few minutes—it is rarely necessary for it to extend beyond 5 minutes.

As mentioned above, the process is advantageously applied to metal articles of all types, for instance sheet metal panels and assemblies, pressings and stampings and machined parts of all kinds, which have been subjected to treatments in an aqueous medium and must thereafter be dried either because they are then in the finished conditions or as a preparation for further treatments, for instance, decorative or protective finishing with paints, enamels, lacquers or varnishes or the like. However, the process is not limited to the treatment of metals in massive form and can be applied, for instance, to the drying of metal powders and also to non-metallic articles which are inert and non-absorbent, for instance, glazed ceramics, glass in various forms including blown glassware, optical lenses and prisms, glass wool or woven glass fabrics, and filaments of non-absorbent materials such as nylon, and polyesters (for instance, "Terylene") and such other polymeric materials as are substantially unaffected by a brief immersion in chlorinated hydrocarbon solvents.

The following examples illustrate, but do not limit, the invention.

Example 1

Bundles of chromium plate furniture hinges each 1½" long and wired together as for the plating process so that a bundle of wires hold five gross of hinges were immersed while wet in boiling trichloroethylene containing 0.25% of cetyl pyridinium bromide for 30 seconds, allowed to drain and then transferred for a further 30 seconds to a bath of clean boiling trichloroethylene. After removal and drying in air they were bright and free from any stain.

Example 2

Oil filters each consisting of a piece of 120 mesh brass gauze in the form of a cylinder 1½" long and ¾" diameter mounted between brass end fittings were loaded into a wire mesh tray 16" x 6" x 2" deep. The filters

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were brightened in the customary manner by immersing them in acid solution and they were then rinsed in running water but on removal from this a quantity of water was retained in the fine mesh gauze. The tray of filters while still wet was immersed for 30 seconds in boiling trichloroethylene containing 0.25% of cetyl pyridinium bromide, allowed to drain, immersed for a further 30 seconds in clean boiling trichloroethylene, again drained and then allowed to dry. No water was retained in the gauze or elsewhere on the filters which had a clean bright appearance, free from stains.

Example 3

Brass wire 0.040" diameter in the form of a coil weighing 80 lb. which had been brightened with acid and rinsed with water as described in Example 2, was immersed for 2 minutes in boiling trichloroethylene containing 0.25% of cetyl pyridinium bromide. It was then drained and immersed in clean boiling trichloroethylene for 2 minutes. Finally it was slowly removed from the bath, being raised at a speed of 2 ft. per minute so as to allow retained solvent to drain away and solvent vapour held in the coil to be displaced by air. On opening out the coil it was found that no water was retained on any of the wire, which was clean and bright and free from stains.

Example 4

A quantity of wet iron powder was stirred into a bath of trichloroethylene containing 0.25% of cetyl pyridinium bromide at room temperature. The liquid was decanted and the powder washed several times with clean trichloroethylene and then spread out on trays where it dried within a few minutes at room temperature. The product was non-oxidised and free flowing.

Example 5

A piece of wet polished stainless steel was dipped into a cold 0.5% solution in trichloroethylene of a cationic surface active agent made by condensing methyl octadecylamine with 4.6 molecular proportions of ethylene oxide. Within 5 seconds the water was displaced from the metal, which was then removed and rinsed with clean trichloroethylene. On evaporation the metal surface was clean, bright and free from stain.

Example 6

Mild steel panels were degreased in trichloroethylene vapour and given a phosphate coating by immersion in:

(a) A proprietary zinc phosphate solution containing nitrate and nitrite accelerators, or

(b) A proprietary zinc phosphate solution containing chlorate accelerator and were then rinsed in cold water. These panels were divided into three batches which were given the following treatments respectively:

(1) Dried in an oven, or
(2) Rinsed in hot water containing 0.025% chromic acid and 0.025% phosphoric acid and dried in an oven, or,

(3) Dried by being immersed in a 0.25% solution of cetyl pyridinium bromide in trichloroethylene, removed, allowed to drain and exposed to the air to allow the solvent to evaporate.

Mains water (total hardness expressed as CaCO_3 320

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parts per million, temporary hardness expressed as CaCO_3 280 parts per million) was used to prepare all phosphating and rinsing solutions. All the panels were then finished with one coat of cross linked vinyl/acrylic enamel as covered by British patent application 12782/58, stoved for 30 minutes at 150°C . and then immersed in water at 40°C . for 50 hours. This is a severe test used to determine the resistance of the paint film to humid or hot and humid conditions of use or storage. At the completion of this test contamination blistering in the form of "tide marks" showed on all panels that had been cold rinsed and oven dried (1). The inclusion of the chromic/phosphoric acid rinse (2) reduced the size and number of blisters but did not eliminate blistering on any panel. With the third "solvent drying" treatment all panels were entirely free from blisters. The tests were made in quadruplicate.

What I claim is:

1. A process for drying water-contaminated surfaces of articles of metal or other non-absorbent material which comprises contacting the said surfaces with a chlorinated hydrocarbon solvent containing dissolved therein 0.001% to 1% by weight of a cationic surface active agent.

2. A process as claimed in claim 1 wherein the solvent is selected from the group consisting of trichloroethylene and perchloroethylene.

3. A process as claimed in claim 1 wherein the cationic surface active agent is present in an amount equal to 0.001% to 0.5% by weight of the chlorinated hydrocarbon solvent.

4. A process as claimed in claim 1 wherein the cationic surface active agent is a quaternary ammonium salt bearing a long chain alkyl substituent.

5. A process as claimed in claim 4 wherein the cationic surface active agent is selected from the group consisting of long chain alkyl pyridinium and trimethyl ammonium bromides and chlorides.

6. A process as claimed in claim 3, wherein the cationic surface active agent is present in an amount equal to 0.1% to 0.3% by weight of the chlorinated hydrocarbon solvent.

7. A process for drying a water-contaminated surface of an article of metal or other non-absorbent material which comprises contacting said surface with a chlorinated hydrocarbon solvent containing dissolved therein 0.001% to 1% of a cationic surface active agent, continuing said treatment until the solvent has displaced the water from the surface of said article, rinsing said surface with a further quantity of said solvent containing no cationic surface active agent, and then evaporating the solvent from said surface.

8. Process as claimed in claim 7 wherein at least the contacting of said surface with the solution of the cationic surface active agent is carried out at elevated temperature.

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