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PROCESS FOR METAL COATING CELLULOSE TRIACETATE

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This invention relates to metal coated membranes. In particular, this invention relates to metal coated plastic film and a method of depositing a metal coating on such plastic film. More particularly, this invention relates to a method of metal coating cellulose triacetate film and such metal coated cellulose triacetate films.

Heretofore, the art has found it exceedingly difficult to metal coat cellulose triacetate films. One method employed was to physically impress finely divided metal powders or fine mesh metal sieves into the surface of a partially polymerized resin or into a material wherein a completely polymerized resin is bound in a thermoplastic resin matrix. In other embodiments, a thermoplastic binder has been employed to cause the metal particles to adhere to a membrane surface. Methods which were tried and proved to be unsuccessful were the dyeing of the surface of the cellulose triacetate film with a dye containing redox groups or ion exchange groups. Such groups were to deposit catalyst cites upon the membrane for the subsequent deposition of a continuous metal coating. Such coating does not adhere to the membrane. The impressing of metal into a partially polymerized surface or using a plastic binder to bind metal particles to the surface of the triacetate film are unsatisfactory wherein the metal coated film is to be used as an electrode or a resistance heater. In order to perform efficiently as a resistance heater or an electrode, a continuous layer of conducting material essential to the transmission of electrons to or from all parts of the coated surface is necessary. It is difficult to achieve this type of continuous coating by impressing the metal powders into the surface of the partially polymerized film or by using a plastic binder to adhere the metal particle to the plastic film.

It has now been discovered that highly effective metal coated cellulose triacetate film may be prepared by coating a thin film with a continuous metal coating. The process involves treating the film first with aqua regia and then contacting the treated film with a silver salt solution. Heretofore, it has been extremely difficult to metal coat cellulose triacetate films with a thin continuous electrically conductive coating of metal. By the instant process, the cellulose triacetate film may be coated with various metals. The process of this invention comprises the first step of treating the film with aqua regia for about 10 to 20 minutes, preferably 13 to 17 minutes and a second step of soaking the treated film in a 20 to 30% solution of silver nitrate and a reducing agent for about 5 to 20 minutes. The second step may be repeated a number of times to insure that there is a continuous coating of the silver metal on the triacetate film.

Once a continuous layer of silver is formed on the film, other materials can be electrically deposited upon the silver by using the silver surface as a cathode in a conventional electrodeposition cell having an electrolyte bath of the desired metal ions such as copper, the noble metals such as platinum, gold, iridium, rhodium and palladium as well as the transition metals such as nickel, chromium, iron and cobalt. Other metals may be chemically exchanged for the silver to provide a continuous metal coating of some metal other than silver. Other metals that may be chemically exchanged for the silver are metals such as platinum, gold, iridium, rhodium and palladium.

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The process of providing a metal surface on a triacetate film by exchanging the metal for silver comprises the steps of (1) treating the triacetate film with aqua regia for 15 minutes, (2) soaking the treated film in a 20 to 30% solution of silver nitrate and a reducing agent for about 6 minutes, (3) treating the triacetate film in a 0.01 molar gold chloride solution, and (4) washing the triacetate film with a silver ion complexing agent in order to remove the excess silver ions. The second and third steps may be repeated a number of times to insure a continuous coating of the metal film.

The reducing agents which can be used in the practice of this invention include hydroquinone, a solution of hydroquinone and gum arabic and a hypophosphite salt. The silver ion complexing agents include ammonium hydroxide and thiosulfates such as sodium thiosulfate and potassium thiosulfate.

A nickel coating may be applied by the same procedure as aforescribed for a silver coating. The acetate film is treated with aqua regia, silver nitrate and then ions of gold, platinum or palladium are applied to the treated surface to establish catalyst cites for the deposition of the nickel. The film containing the catalyst cites is then contacted with an aqueous solution containing nickel ions and a reducing agent such as a hypophosphite salt, particularly sodium or potassium hypophosphite. This embodiment is preferably carried out at temperatures between 60 to 95° C.

The metal coated cellulose triacetate films prepared by this process may be used as electrodes in a fuel cell or electrochemical cell and/or as dividers to divide a cell into two or more compartments or may be used as the heating element in resistance heaters. That is, the electrical current may be induced into the metal foil causing it to heat and radiate heat therefrom. Such heaters may be used in the building trade, that is, large sheets of metal coated cellulose triacetate may be placed behind the walls to be used as radiators of heat. A metal coated film of this invention can serve as both an anode or cathode in a fuel cell which used either an acidic or basic electrolyte. It is, of course, obvious to those skilled in the art that when using an acid electrolyte that the metals deposited upon the cellulose triacetate film must be nonreactive with the acid electrolyte. Therefore, metals such as nickel and copper could not be used. However, the noble metals would be very useful. The following examples are illustrative of the process of this invention and should not be construed as limitations upon the true scope of this invention as set forth in the specification and claims.

Example 1

A 100 square inch cellulose triacetate film was immersed in aqua regia for 15 minutes. The film was then soaked in 150 cc. of 25% silver nitrate for 15 minutes. The film was removed and soaked in a bath containing 10 cc. of 25% silver nitrate in a 150 cc. solution of 15 grams per liter hydroquinone and one gram per liter gum arabic for 5 minutes. The film was removed from this solution after 5 minutes, washed with distilled water and then soaked in identical solution of silver and hydroquinone for 5 minutes. The resulting silver coated membrane was tested and found to be flexible and a good electrical conductor.

Example 2

A silver coated membrane prepared in accordance with Example 1 was immersed in an electrodeposition bath containing iron ions. The silver coated film was the cathode in the electrodeposition bath. The iron was electrically deposited upon the silver coating of the film. The iron coated film was removed from the bath. The

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film was found to have a continuous coating of iron thereon and testing proved the iron coating to be firmly adhered to the cellulose triacetate film.

Example 3

A silver coated film prepared in accordance with Example 1 was immersed in a 0.02 molar solution of gold chloride for 20 minutes. The gold during this time replaced the silver of the silver coating thereby providing a gold coated film. The film was removed from the gold bath and tested. The test determined that the metal coating was firmly adhered to the cellulose triacetate film and was electrically conductive.

Example 4

A 100 square inch cellulose triacetate film was immersed in aqua regia for 15 minutes. The film was then soaked in 150 cc. of 25% silver nitrate for 15 minutes. The film was then removed and soaked in a bath containing 10 cc. of 25% silver nitrate in a 150 cc. solution of 15 grams per liter hydroquinone and 1 gram per liter gum arabic for 6 minutes. The film was removed from this solution, washed with distilled water and then soaked in identical solution for 5 minutes. After the second soaking the film was removed, washed with distilled water and soaked in a 50 cc. solution of 0.01 molar gold chloride. The film was removed from the gold chloride bath and washed with 50 cc. of NH_4OH and in 50 cc. of distilled water. The ammonia washed film was then immersed in an aqueous solution of nickel chloride and sodium hypophosphite with a sodium acetate buffer until a continuous layer of nickel was formed. The acetate film was left in the nickel bath for about 9 to 11 minutes. The nickel coated film thus produced was tested and found to be continuous, electrically conductive and firmly bound to the cellulose triacetate film.

What is claimed is:

1. A process for metal coating cellulose triacetate plastic film which comprises the steps of
 - (a) contacting cellulose triacetate plastic film with aqua regia for about 10 to 20 minutes, and
 - (b) soaking the film prepared in step (a) in a solu-

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tion of a noble metal salt and a reducing agent to deposit a continuous metal coating on said film.

2. A process as defined by claim 1 wherein said reducing agent is selected from the group consisting of a hydrophosphite salt and hydroquinone.

3. A process as defined by claim 1 wherein said reducing agent is hydroquinone.

4. A process as defined by claim 1 wherein said noble metal salt is silver nitrate.

5. A process for metal coating cellulose triacetate film which comprises the steps of

(a) contacting cellulose triacetate plastic film with aqua regia for about 10 to 20 minutes,

(b) soaking the film prepared in step (a) in a solution of a noble metal salt and a reducing agent to deposit a continuous silver coating on said film,

(c) soaking the film prepared in step (b) in a solution comprising about 0.01 molar gold chloride to replace said silver coating with a continuous coating of gold,

(d) washing the film prepared in step (c) with a solution comprising a silver ion complexing agent to remove excess silver ions, and

(e) immersing the film prepared in step (d) in a solution comprising a reducing agent and a metal salt selected from the group consisting of silver salts and nickel salts to deposit a continuous metal coating on the film.

6. A process as defined by claim 5 wherein said complexing agent is ammonium hydroxide.

References Cited by the Examiner

UNITED STATES PATENTS

35	1,529,712	3/1925	Pfiffner	117—60
	2,278,722	4/1942	Loiseleur	117—47
	2,430,581	11/1947	Pessel	117—160 X
	2,757,104	7/1956	Howes	117—213 X
	2,934,457	4/1960	Elliott	117—47
40	3,179,575	4/1965	Dippel et al.	117—217 X
	3,235,473	2/1966	Le Duc	117—47

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