

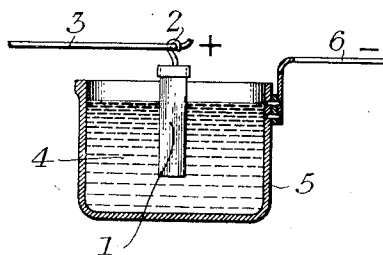
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ELECTRODEPOSITION OF COATINGS OF CELLULOSIC COMPOUNDS

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ELECTRODEPOSITION OF COATINGS OF CELLULOSIC COMPOUNDS.

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This invention relates to the deposition of cellulosic compounds onto conducting surfaces of objects. One object of the invention is to provide a process by which one or more cellulosic compounds may be quickly and inexpensively deposited upon articles having a conducting surface. Another object is to provide a process in which the deposited cellulosic compound or compounds will have associated therewith coalescing agents by means of which the deposited particles unite into a suitable coating. Another object of the invention is to provide a process of coating with cellulosic compounds without the excessive fire hazard which attends the use of their solutions in inflammable solvents. Other objects will hereinafter appear.

In the accompanying drawing, forming a part hereof, the single figure is a diagrammatic cross section of an apparatus which may be employed in carrying out our process.

We have found that useful coatings of one or more cellulosic compounds may be electrodeposited upon conducting surfaces of objects by utilizing electroconducting emulsions of such compounds. We have also found that the deposited particles of cellulosic compound will unite into a coating having the desired properties if a suitable solvent or coalescing agent is present in the droplets, or in the liquid containing the droplets, or both. We shall now give by way of example, one embodiment of our invention. It will be understood that the invention is not restricted to this example, or to the details thereof, except as indicated in the appended claims.

In the following illustration we dissolve the cellulosic compound in a liquid which includes a coalescing agent, and then emulsify the solution in an aqueous bath containing a suitable emulgent and also preferably containing a protective colloid. We may, for example, dissolve 500 parts of cellulose nitrate, say of the kind used for films or the kind used for low viscosity lacquers, in 1500 parts by weight of amyl acetate. Next we mix 10 parts of the protective colloid, say gum arabic, for instance, and 150 parts by weight of an emulgent, say 150 parts of Turkey Red oil, into 10,000 parts of water. The solution of nitrate in

amyl acetate is then mixed into the aqueous bath containing the emulgent and colloid. The mixing is effected by thorough stirring or other suitable agitating process.

The above described operations give a preliminary emulsion which is useful by itself for electrodeposition. We have found that it is desirable to make the droplets of the emulsion of a more nearly uniform size. This enables the electrodeposition to be conducted better and gives a more stable emulsion. We, therefore, prefer to homogenize the above described preliminary emulsion by running it through a high-speed colloid mill, any of the well known ones which are on the market being useful for this purpose. The action of the mill is regulated to bring the droplets down to a small size, most of them having about the same order of magnitude. The emulsion is more stable if it is slightly alkaline. In any event we, of course, prefer to avoid sufficient acidity to cause coagulation of the emulsion. If desired, a small amount of alkali can, therefore, be present in the aqueous bath when the solution of cellulosic compound is mixed into it to effect the preliminary emulsification.

In place of the cellulose nitrate solution, when preparing the above emulsion, we can substitute a solution of cellulose acetate, for example 500 parts of chloroform-soluble cellulose acetate dissolved in 1500 parts of chloroform or acetylene tetrachloride. Similarly we can use 500 parts of acetone-soluble cellulose acetate dissolved in 1500 parts of acetylene tetrachloride. The cellulose ether, such as water-insoluble ethyl cellulose, may be dissolved in a mixture of equal parts of benzol and ethyl alcohol, say 500 parts of the ether and 1500 parts of the solvent mixture. Moreover, mixtures of these cellulosic compounds in common solvents may be stirred into the aqueous bath, so as to form emulsions, the droplets of which contain a plurality of cellulosic compounds, or separate emulsions of different compounds may be first prepared and then mixed together, yielding a final emulsion in which there are particles of one cellulosic compound and other particles containing a different cellulosic compound.

It will be noted that the liquids in which we dissolve the cellulosic compounds contain

ingredients, such as amyl acetate, chloroform, acetylene tetrachloride, and benzol, which are practically insoluble in water. This causes them to remain in the droplets of the emulsions in useful quantities. When the droplets are electrodeposited there is sufficient of this solvent present to act as a coalescing agent. In other words the particles can be brought together into a strong, uniform or blended coating.

While we prefer to use solvent liquids containing a coalescing agent which is insoluble in water, nevertheless, it is possible to employ solvents which are miscible with water. Thus acetone may be employed to dissolve the nitrate or the acetate, or both together, before emulsification. The amount of such solvent, which passes into the aqueous bath, must, of course, be kept below a concentration which will impair the deposited coating. But, by keeping the concentration sufficient to have a softening effect on the coating the particles of the latter coalesce or blend together. In this way acetone in the bath can act as a coalescing agent. In fact we may have a coalescing agent in the aqueous phase and another, at the same time in the disperse phase. For all ordinary purposes, however, we find it satisfactory to have the coalescing agent in the droplets.

While we prefer the above mentioned emulgent, equivalent materials, such as soaps, phenolates, etc., may be wholly or partially substituted. In place of the protective colloid mentioned above, any other one having similar properties may be used, such, for example, as gelatin and glue.

One or more pigments, like lampblack, for example, may be introduced into the emulsion, either by wetting it and mixing it with the completed emulsion or preferably mixing it into the initial solution of the cellulosic compound. Likewise agents which improve the qualities of the coating may be introduced into the emulsion, say by addition to the initial solution of cellulosic compound. Thus camphor, monochloronaphthalene, triphenyl phosphate, tricresyl phosphate, and the like may be introduced into said solution in amounts which bear to the nitrocellulose the customary ratio which they bear in lacquer or film compositions. Substances of this type which increase the flexibility of the coating are customarily referred to as softeners. Preferably the coalescing agent is a common solvent of both the cellulosic compound and the softener.

The droplets in the emulsion act as if they were negatively charged. They, therefore, travel toward the anode. Referring to the drawing, the electroconducting surface 1 to be plated is connected at 2 to anode 3 to form the anode and is immersed in the emulsion 4. A suitable cathode is also placed in contact with the emulsion. For instance, the

latter may be contained in a metal vessel 5 which is connected with the circuit in the cathode 6. The current should be an effectively unidirectional one. It may be a direct current of constant value, or a direct current of pulsating character. For some purposes it may be convenient to employ a considerably unbalanced alternating current. We prefer, however, to use an ordinary direct current at a voltage of about the order of magnitude of 110 volts. This is especially convenient because it is readily obtainable. The deposition can take place slowly at much lower voltages and more speedily at much higher voltages. But with a flow of approximately $\frac{1}{3}$ of an ampere per square inch of anode surface, with a voltage of 110, the deposition takes place very satisfactorily. Deposition at room temperature is preferred; but if the temperature rises, say because of the consumption of electric energy, no harmful results will be noted. Under the conditions indicated the time of coating is very short, being of the order of magnitude of about 4 minutes; though, of course, this can be varied in accordance with the thickness of the coating desired.

When the surface has a coating of the desired thickness, it may be removed from the bath and washed with water. In the preferred form of our invention the coalescing agent in the deposited particles has caused them to blend into a coating during the plating. The coating is allowed to set or harden, say by evaporation of some of the coalescing agent from it. This setting action can be accelerated by heating. In fact the coating can be treated in any way in which coatings of cellulosic compounds are usually treated. In case the deposited particles of cellulosic compound are not properly blended by the amount of coalescing agent which is present, they can be brought together by special treatment, say by mild mechanical action with a brush or by bathing in a bath containing a suitable coalescing agent, or by both.

Our process is applicable not only to the coating of entire metal articles by electrodeposition, but it can be applied to any article having an electroconducting area on its surface or periphery. The conducting surface does not have to be metallic, for non-conducting objects, such as wood, for example, may be made sufficiently conducting to serve as anodes for receiving the deposition by coating them superficially with a conducting layer, such as graphite, or by impregnating them with solutions of electrolytes. The latter expedient, moreover, is especially adaptable to the coating of fabrics and paper, or other porous non-conducting sheets. These can be impregnated with electrolytes and located over or in contact with the anode between it and the cathode.

The amount of emulsifying agent that remains in the deposit does not in general impair it, the final coating being for ordinary purposes as useful as those prepared in other ways. Where the minimum amount of mineral matter is desired in the deposit, for instance, when its electrical resistance is to be emphasized, the emulsifying agent may be in the form of an ammonium soap. The ammonia can be split off and driven away by heating to a temperature which will not impair the coating.

During the deposition various plating expedients may be employed. It is desirable that the surfaces to be coated with a permanent or adherent layer be clean. They can, for instance, be degreased by heat or suitable solvents, as is well known.

Having thus described our invention, what we claim as new and desire to secure by Letters Patent is:

1. The process of depositing a cellulosic compound on an electroconducting surface of an object, which comprises the steps of bringing said surface into contact with an electroconducting emulsion containing droplets of the cellulosic compound and passing a depositing electric current through said surface and emulsion.

2. The process of depositing a cellulosic compound onto an electroconducting surface of an object, which comprises the steps of bringing said surface into contact with an aqueous electroconducting emulsion containing droplets of cellulosic compound and passing an effectively unidirectional depositing electric current through said surface and emulsion in the presence of a coalescing agent.

3. The process of depositing a cellulosic compound onto an electroconducting surface of an object, which comprises the steps of bringing said surface into contact with an electroconducting aqueous emulsion containing droplets of mixed cellulosic compound and coalescing agent and passing an effectively unidirectional depositing electric current through said surface and emulsion.

4. The process of depositing a cellulosic compound and a softener onto an electroconducting surface of an object, which comprises the steps of bringing said surface into contact with an electroconducting aqueous emulsion containing droplets of said cellulosic compound and softened, and passing an effectively unidirectional depositing electric current through said surface and emulsion.

5. The process of depositing a cellulosic compound and a softener therefor onto an electroconducting surface of an object, which comprises the steps of bringing said surface into contact with an electroconducting aqueous emulsion containing in the droplets cellulosic compound, softener and a coalescing

agent which is a common solvent of said compound and softener, and passing an effectively unidirectional depositing electric current through said surface and emulsion.

6. The process of depositing a colored cellulosic compound onto an electroconducting surface of an object, which comprises the steps of bringing said surface into contact with an electroconducting aqueous emulsion containing colored droplets of cellulosic compound, and passing an effectively unidirectional depositing electric current through said surface and emulsion.

7. The process of depositing colored cellulosic compound and a softener therefor onto an electroconducting surface of an object, which comprises the steps of bringing said surface into contact with an electroconducting aqueous emulsion containing droplet having therein said cellulosic compound, said softener and a coloring agent, and passing an effectively unidirectional depositing electric current through said surface and emulsion.

8. The process of depositing a cellulosic compound onto an electroconducting surface of an object, which comprises the steps of bringing said surface into contact with an aqueous electroconducting emulsion containing an emulsifying agent, droplets of said cellulosic compound and a protective colloid, and passing an effectively unidirectional depositing electric current through said surface and emulsion.

9. The process of depositing a cellulosic compound onto an electroconducting surface of an object, which comprises the steps of immersing said surface in an aqueous electroconducting emulsion containing an emulsifying agent, a protective colloid and droplets of said cellulosic compound having therein a coalescing agent, and passing an effectively unidirectional electric current through said surface and emulsion in a direction to deposit said droplets onto said surface.

10. The process of covering an electroconducting surface with a set coating of a cellulosic compound which comprises bringing said surface into contact with an electroconducting aqueous emulsion containing droplets of said cellulosic compound, and passing an effectively unidirectional electric current through said surface and emulsion in the presence of a coalescing agent in a direction to deposit said droplets into a coalescing coating on said surface, and causing said coating to set.

11. The process of covering an electroconducting surface with a set coating of a cellulosic compound, which comprises bringing said surface into contact with an electroconducting aqueous emulsion containing droplets of said cellulosic compound having therein a coalescing agent, and passing an

effectively unidirectional depositing electric current through said surface, and emulsion to form a coalescing coating of said cellulosic compound on said surface, and causing said coating to set.

12. The process of depositing nitrocellulose on an electroconducting surface of an object, which comprises the steps of bringing said surface into contact with an aqueous electroconducting emulsion containing an emulsifying agent and droplets of nitrocellulose, and passing a depositing electric current through said surface and emulsion.

13. The process of depositing nitrocellulose on an electroconducting surface of an object, which comprises the steps of bringing said surface into contact with an electroconducting aqueous emulsion containing droplets of nitrocellulose and a protective colloid, and passing a depositing electric current through said surface and emulsion.

14. The process of depositing nitrocellulose as a coating on an electroconducting surface of an object, which comprises the steps of bringing said surface into contact with an aqueous electroconducting emulsion containing droplets of nitrocellulose having therein a coalescing agent insoluble in water, and passing a depositing electric current through said surface and emulsion.

15. The process of depositing nitrocellulose on an electroconducting surface of an object, which comprises the steps of bringing said surface into contact with an electroconducting aqueous emulsion containing

droplets of nitrocellulose and amyl acetate, and passing a depositing electric current through said surface and emulsion.

16. The process of depositing nitrocellulose on an electroconducting surface of an object, which comprises the steps of bringing said surface into contact with an electroconducting aqueous emulsion containing gum arabic, sulfonated castor oil, and droplets having therein a mixture of nitrocellulose and amyl acetate.

17. The process of depositing a cellulosic compound on an electroconducting surface of an object, which comprises the steps of bringing said surface into contact with an electroconducting aqueous emulsion containing droplets of said cellulosic compound and passing a depositing electric current through said surface and emulsion, the current density being of the order of $\frac{1}{3}$ ampere per square inch of said conducting surface.

18. The process of depositing a cellulosic compound on an electroconducting surface of an object, which comprises the steps of bringing said surface into contact with an electroconducting emulsion containing droplets of said cellulosic compound and passing a depositing electric current through said surface and emulsion at a potential of the order of magnitude of 110 volts.

Signed at Rochester, New York, this 2nd day of April 1925.

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