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PROCEDURE FOR THE FORMATION OF A COATING ON AN OBJECT  
BY POLYMERIZATION BY LUMINESCENT DISCHARGE

Metal Containers Limited

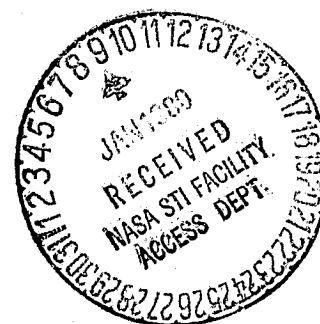
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PROCEDURE FOR THE FORMATION OF A COATING ON  
AN OBJECT BY POLYMERIZATION BY LUMINESCENT DISCHARGE

Metal Containers Limited  
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This invention concerns a procedure for the formation of a 1  
coating on an object by polymerization by luminescent discharge. It  
concerns the obtained coated object as well as a separate article  
obtained by removing the formed coating from the object.

The luminescent discharge is a self-sustained stable discharge  
in gas with relatively low current density and relatively high poten-  
tial gradient, which is produced in low pressure gas by using alter-  
nating or continuous current. In the case of inorganic gas, we ob-  
tain self-sustained luminescence when we use a resistance which limits  
the current in the external electrical circuit. When organic sub-  
stances are present in the luminescent discharge area, generally,  
there is a formation of solid deposits whose behavior and composition  
vary as a function of the operating conditions of the luminescent  
discharge. The deposits are generally polymers of materials which  
were originally monomeric or polymers of intermediary reactive  
products of materials originally monomeric. We have found that,  
in accordance to the known procedure for the formation of a coating  
on an object by polymerization by luminescent discharge, we have  
often obtained coatings whose properties were not satisfactory. For  
example, in certain cases it is desirable to obtain a sticky coating.  
A sticky coating can, for example, be used as an adhesive coating  
which with little pressure or no pressure at all can form a bonding  
between metals, synthetic materials, paper, or any other substrate  
which is flexible or pliable. Sticky coatings can also be used as  
adhesives for the formation of laminated or foliated materials. They  
can be used as a base for printing or as an auxiliary agent which  
improves under pressure sealing. The application of an adhesive film  
with a certain configuration for strong/weak adherence areas can also  
be developed.

In addition, we have found that coating formed on an object by

established procedures of polymerization by luminescent discharge often have the disadvantage of changing color and/or to be brittle. Another inconvenience of coatings produced until now resides in the fact that sometimes they are altered by exposure to air, since the polymerisat which makes up the coating is negatively affected by the oxygen in the air.

Finally, we have found that when the coating must be then separated from the object on which it has been placed in order to form a separate article, it is often difficult to carry out such separation without tearing or damaging the formed coating. The object of this invention is to obtain a coating without the disadvantages mentioned above. Another objective of the invention is the formation of a sticky coating suited for the special uses which have been mentioned. Another objective is the formation of a coating which does not show change of tint or discoloration and/or is brittle. Another objective is to treat the formed coating so that the final coating 2 does not show any substantial alteration by exposure to air. Another objective of the invention is the production of a coating by polymerization by luminescent discharge which can be separated from the substrate on which it has been formed without tearing or damaging it. Finally, a last objective of the invention is the manufacture of sticky coating which can be separated from the substrate without any damage and which are not altered by exposure to air.

In view of these objectives, the invention gives a procedure for the formation of a coating on an object by polymerization by luminescent discharge which consists of the placing of this object in a reaction area located in a luminescent discharge chamber, introducing a polymerizable material in this reaction area and applying an electrical field to this reaction area by means of an electrode and a counter-electrode in order to produce a luminescent discharge directed toward the object and to obtain a polymerized matter coating on this object under controlled conditions. In order to improve the properties of the coating, when desired, the produced coating is subjected to further treatment to protect it against alteration by exposure to air. The polymerizable material can be in the form of vapor or gas; it can also have low volatility and it can also be

introduced by atomization or spraying of droplets and/or of solid particles in the reaction area, as described in the British request for patent number 13.408/65.

When the polymerizable material is not a vapor or a gas, it can be introduced in the reaction area in the melted or dissolved state.

It must be noted that the term "place" must not be understood as limiting the invention to the formation of a coating on a fixed object. On the contrary, this object can be made to cross the reaction area continuously or intermittently. This way, for example, it is possible to coat continuous bands.

It must also be clear that the above description of the invention does not indicate a mandatory succession of the various stages which make up the procedure according to the invention. These stages can be carried out in any arbitrary, appropriate succession or they can be carried out simultaneously without leaving the framework of the invention.

It is possible to introduce an ionizable non-polymerizable gas in the reaction area or to keep an atmosphere containing an ionizable non-polymerizable gas in the reaction area to start and/or to maintain and/or to help the luminescent discharge.

There can be several ways of obtaining the controlled conditions mentioned above. For example, the sticky coating can be manufactured by placing an object in the reaction area and by operating with a rate of introduction of the polymerizable material in the reaction area which exceeds the polymerization speed, with the result that we have the formation of a sticky coating incompletely polymerized. Sticky coatings of this kind can harden later, for example, when exposed to air.

A high frequency luminescent discharge near the object to be coated is particularly useful for obtaining sticky coatings. Preferably, we should use an alternating electrical current source with a frequency greater than 500 kilocycles per second.

Discoloration or tint modification and/or the brittle nature of the coating can be avoided, preferably, by artificial cooling of the object to be coated. The object can be cooled before and/or during

the application of the coating on this object. If the object constitutes the counter-electrode of the discharge system, the object-counter-electrode combination is cooled artificially. When the object is between the electrode and the counter-electrode, for example, when the object is made of a non-conductive material, it can be placed in direct contact with the counter-electrode and the counter-electrode can be cooled artificially. The object is therefore cooled indirectly by the intermediary action of the counter-electrode.

Laminations can be produced by uniting the surfaces of two or several films or sheets made of plastic or paper in the luminescent discharge chamber, some of these sheets or films or their combinations having been provided with a sticky coating by luminescent discharge. This can be accomplished by simply rolling together the sheets or bands on a winding roll and/or making them pass through rollers.

The formation of laminations can also be carried out outside the luminescent discharge chamber but it is necessary that two sheets leave the chamber vacuum-tight. Furthermore, the sticky nature of these sheets can deteriorate when they are exposed to the external atmosphere. Because of this, internal lamination formation is preferred.

To obtain a coating of a polymerized material which is not influenced negatively by exposure to air, particularly by the oxygen in the air, the coating formed in the reaction area is placed in 3 contact, in a second area, with a reactive fluid which can be liquid or in the form of vapor or gas. Preferably the coating is placed in contact with the fluid in the second area just before the end of the polymerization. This way, the final stage of the polymerization procedure can be controlled and the properties of the coated material can be greatly improved. The flexibility of the material can be improved most.

The expression "to place the coating in contact in the second area" does not mean necessarily the physical displacement of the coating from the reaction area toward or in the second area. From the "environment conditions" point of view, a change can be made by removing the atmosphere present in the reaction area and replacing this atmosphere with the reactive fluid while interrupting or stopping

the luminescent discharge. The coating can be moved from the first area toward the second area together with the object on which it has been formed. The coating can also be removed from the object in order to form a distinct manufactured article. This can be done after termination of the complete procedure but in a particular procedural mode, the separation of the coating from the object takes place before or during displacement of the coating from the first area to the second area.

As a reactive fluid, we can use a substance capable of reacting with residual reactive substituents in the coating. Preferably, we should use a reactive fluid which constitutes a good acceptor of free radicals. For example, we can use a reactive fluid consisting of nitrogen dioxide or containing this product. As a variation, we can use a reactive fluid consisting of water vapor or containing water vapor. We can also obtain good results by using a reactive fluid consisting of an alcohol such as methanol or containing an alcohol.

It is also possible to use a reactive fluid consisting of a substance or containing a substance which produces a colored layer of deposits on the surface of the coating at the same time when we set up the post-coating polymerization. We can also use a reactive fluid consisting of a substance or containing a substance capable of reacting on the surface of the coating by forming a colored layer at the time the polymerization of the post-coating is set. As a variation or in addition to one or several of the stages described above regarding the treatment of the coated surface, we can add another monomer, for example a vinyl monomer such as methacrylate to the polymer of the coating so that it acts as a plastifying agent or it modifies and improves the properties of the coating.

The reactive fluid can be made up of the same monomer or it can contain the same monomer which was used in the stage of polymerization by luminescent discharge. Appropriate reactive fluids are styrene, methyl methacrylate or acrylonitrile.

The later treatment in the second area can be regulated by controlled heating and/or by applying pressure as to permit the establishment of optimal conditions for the coating procedure. The procedure can be used for the formation of protective or insulating

coatings on a great variety of objects such as, for example, containers, tubes, sheets, tissues, wires, filaments, etc. The stage of removal of the coating from the object in order to form a distinct manufactured article can also be part of the invention procedure. This way, the invention procedure can be utilized for the production of films, sheets, bands, tubes, sacks, fittings, or container coatings, self-supporting containers and/or accessories for the above mentioned products as well as for any other article in a great variety of manufactured articles.

The removal of the coating from the object in order to form a separate manufactured article can be carried out in any appropriate manner, for example, by "cutting out the coating from the object," when manufacturing sheets, films, sacks, and similar articles. Coating removal can be facilitated by exposing the coated object to the action of a suited organic solvent which does not damage the coating.

The object on which the permanent or temporary coating is formed can be made of any desirable and appropriate material, such as, metal, wood, paper or cardboard, glass, a thermoplastic or thermohardening material, etc.

The polymerizable material to be used in the procedure can be an organic material, mineral material, and organo-mineral material such as an organo-metallic material.

When manufacturing films or long thin articles by formation of a coating of polymerized material on a substrate by polymerization by luminescent discharge and subsequent separation of the above mentioned coating from the substrate, we have encountered, at times, some difficulties in obtaining a separation without tearing or damaging the coating formed on the substrate. In accordance with one aspect of the invention, we can effectively solve this problem by using a liquid as the substrate on the surface of which the temporary coating is formed; preferably, we should use a liquid which adheres little to the coating or to the film formed on its surface. In most cases the liquid substrate is the counter-electrode.

The material for the liquid electrode can be a metal such as mercury or gallium an alloy, according to the temperature of the liquid

solution in question.

The coating formed on the surface of the liquid electrode can be removed in a continuous manner. In this case, it is preferably removed at uniform speed, so that the article is removed as it is produced and as it reaches the desired predetermined thickness. As a variation, the coating can be removed from the surface of the liquid electrode intermittently in order to produce sheets of a desired predetermined length and width corresponding to the length and width of the liquid electrode solution. It is naturally possible to combine one or several of the above mentioned conditions. It is then possible to produce a coating by using the high frequency luminescent discharge near an artificially cooled object. The coated object or the coating as a separate manufactured article can be placed if so desired, in a second area containing a reactive fluid such as described above. A coating separated from the liquid substrate can also be placed in a second area of this kind. Various other modifications and variations can be made without leaving the framework of the invention.

#### Summary

The objective of this invention is:

A. A procedure for the formation of a coating on an object by polymerization by luminescent discharge characterized by the fact that the object is placed in a reaction area located in a luminescent discharge chamber that a polymerizable material is placed in this reaction area and an electrical field is applied to this reaction area by means of an electrode and a counter-electrode, with the resulting production of a luminescent discharge toward the above mentioned object and the obtainment of a polymerized material coating on this object under controlled conditions which include the properties of the coating; when desired, the manufactured coating may undergo a post-treatment to protect it from alterations through exposure to air.

The procedure can have the following features, either by themselves or in all their technically possible combinations:

1. We utilize a high frequency luminescent discharge;
2. We utilize an alternating source of electrical current with a frequency greater than about 500 kilocycles per second;
3. The object to be coated is cooled artificially;
4. The object to be coated constitutes a counter-electrode, which is cooled artificially;
5. The object to be coated is placed in direct contact with a counter-electrode, which is cooled artificially;
6. The coating is formed on the surface of a liquid substrate;
7. We utilize a liquid counter-electrode on the surface of which a coating is formed;
8. The manufactured coating is removed from the object;
9. The coating manufactured in the reaction area is placed in contact, in a second area, with a reactive fluid which can be liquid, in the form of vapor or gas;
10. The coating is placed in contact with the fluid in the second area just before the end of polymerization;
11. The present atmosphere is eliminated from the reaction area and is replaced by a reactive fluid thus interrupting the luminescent discharge and creating the second area;
12. We utilize a reactive fluid which can react on the residual reactive substituents in the coating;
13. We utilize a reactive fluid which is a good acceptor of free radicals;
14. We utilize a reactive fluid which is made up of nitrogen dioxide or which contains nitrogen dioxide;
15. We utilize a reactive fluid which is made up of water vapor or which contains water vapor;
16. We utilize a reactive fluid which is made up or which contains an alcohol such as methynol;
17. We utilize as a reactive fluid styrene, methyl methacrylate or acrylonitrile;
18. We utilize a reactive fluid which is made up of a substance producing a colored layer on the coating or containing such a substance.

B. As a new industrial product, a manufactured article consist-

ing of a coated object produced through the procedure specified in 25  
A.

C. As a new industrial product, a manufactured article obtained by the formation of a coating on an object by the procedure specified in A., and by removal of this coating from the object.