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TREATMENT FOR INCREASING THE HYDROPHILICITY OF MATERIALS

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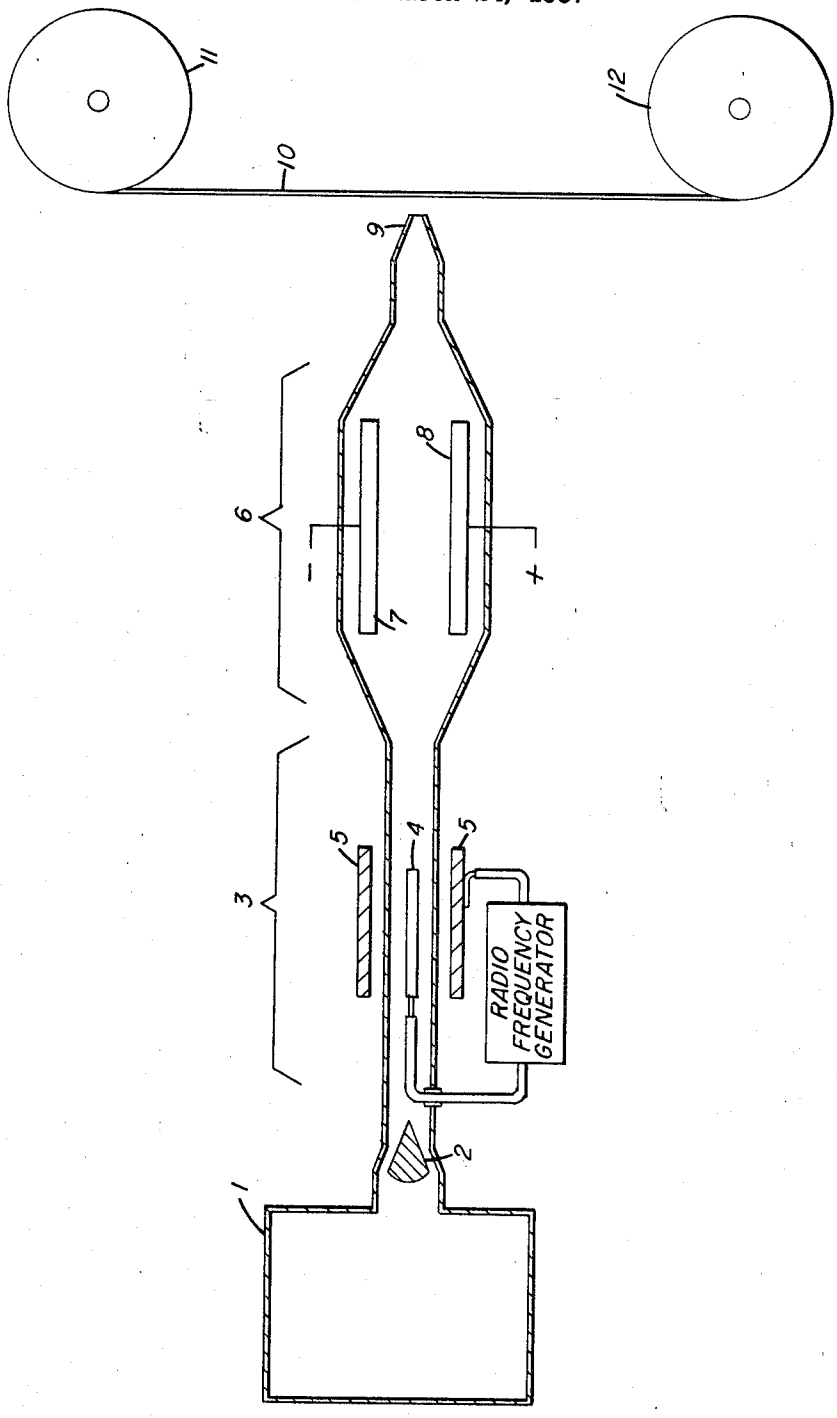

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TREATMENT FOR INCREASING THE HYDROPHILICITY OF MATERIALS

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ABSTRACT OF THE DISCLOSURE

Method and apparatus for rendering hydrophilic the surface of materials, including normally hydrophobic materials: a gas is electronically excited to produce an activated species which is then passed through an ion trap, to remove charged particles therefrom, and blown across the surface to be treated.

BACKGROUND OF THE INVENTION

This invention relates to the treatment of the surface of materials, including normally hydrophobic materials, for rendering such surfaces hydrophilic in order that they may be more receptive to inks, adhesives, or other coatings.

Such treatment is well known, particularly in relation to polymers such as polyethylene. In earlier prior art relating to this matter, hydrophilicity was produced by treating such surfaces with open flames, but more recently the prevalent method has been to submit the surfaces to corona discharge. However, all presently known prior art methods are not fully satisfactory for several reasons, e.g.: heat-treating often deforms the material being treated; corona discharge often causes pinholes in the material; electrostatic charges are induced in the material, raising many problems for post-treatment handling; and unusually shaped articles, such as bottles, balls, etc. cannot be treated in a reliable manner.

In some more recent attempts to improve upon the corona discharge systems, the discharge is not directed through the material but rather through a path adjacent the surface to be treated. Also, gentle streams of air or other gases have been used to deflect the corona arc so that it does not damage the material being treated. Nonetheless, even these improved prior art systems still result in occasional damage to the surface being treated due to the action of charged particles, and the post-treatment problems relating to charges induced in the web have not been overcome.

During experimentation relating to the corona discharge treatment referred to above, it was found that a stream of air directed across the discharge area substantially increased the resulting area of hydrophilicity in the direction of the air flow. Further experimentation was undertaken to determine what effect jets of different types of gases would have in this expansion of the effective area of the corona treatment, and oxygen, nitrogen and helium were all blown through and across the corona discharge treatment area. It was found that nitrogen and helium were more effective in producing a hydrophilic surface than air or oxygen by many orders of magnitude, and this finding led directly to the conception of the invention herein.

SUMMARY OF THE INVENTION

The problems referred to above are avoided by the improved method and apparatus disclosed herein which does not subject the material to either an elevated temperature, open flames, or electrical discharge. It has been found that normally hydrophobic surfaces are rendered

hydrophilic when bathed in a stream of an activated species of a gas. According to the invention herein, a gas such as helium or nitrogen, is excited electronically to produce an activated species. Some ionization may occur during the electronic activation of the gas, and since it is often desirable to eliminate the possible electrostatic effects of such ionized particles, a preferred embodiment of the invention employs an ion trap. In such embodiment, the activated species is first passed through an ion trap to remove any charged particles and, thereafter, is delivered in a stream to the surface being treated. This novel and simple treatment has not only been used successfully to render hydrophilic the surface of normally hydrophobic polymers, it has also been used to increase the hydrophilicity of paper and metal.

Therefore, it is an object of this invention to provide a simple and economical method for rendering materials hydrophilic.

It is a further object of this invention to render materials hydrophilic without the use of heat, flame or corona discharge.

These and other objects, purposes and characteristic features of the present invention will be in part obvious from the accompanying drawing, and in part pointed out as the description of the invention progresses. In describing the invention in detail, reference will be made to the accompanying drawing which illustrates, in schematic cross-section, simple apparatus which may be used to carry out the invention herein.

Referring now to the drawing, a gas (such as argon, helium, hydrogen, krypton, neon, nitrogen, or xenon) is released from pressurized reservoir **1** through valve **2** to an exciter stage **3**. This exciter stage is comprised of electrode **4** and a surrounding plate **5** between which a relatively high potential radio frequency field is maintained to cause a continuous discharge of electrons from the surface of electrode **4**. This electron activity causes a portion of the gas passing through this section of the apparatus to be excited to a higher energy level, thereby forming an activated species. The gas next passes through an ion trap **6** comprising oppositely charged plates **7** and **8** which attract any charged particles which may have been formed during the electronic excitation stage. The electrically-neutralized, activated species of the gas is then delivered through nozzle **9** against the surface of web material **10** which is moved past the treatment area by supply and take-up reels **11** and **12**, respectively.

Special attention is called to the following important features of the novel method and apparatus which have just been described: The web **10** is not subjected to any great temperature increase during treatment, and therefore web deformation is avoided. Further, since the electrical field is remote from the surface being treated, the web is not subjected to any electrical discharge, eliminating scouring or pinholing of the surface being treated. Still further, if the ion trap is used the web is not contacted by, nor does it pass in proximity to, either charged particles or electrodes, and therefore there is no buildup of undesirable charges in the web, simplifying handling and storage problems after treatment. Finally, it can readily be appreciated that unusually shaped articles of varying thicknesses and dimensions may be treated effectively by placing them in the path of the electrically-neutral stream of activated species emitted by nozzle **9**.

To facilitate practical apparatus design, it should be noted that the effectiveness of the active species in producing the desired hydrophilicity declines exponentially with the distance over which it is transported, and that its effectiveness is also lost upon collision with a large mass.

The following specific examples provide further illustration of the invention.

Example 1

The following apparatus was assembled to demonstrate that an electrostatically neutral but chemically active species, which is generated in a number of different gases when they are passed through an electrical discharge, is capable of modifying the surface of a number of different materials causing them to become more hydrophilic. The apparatus consisted of a source of pure gas, an excitation chamber, an ion trap, and a sample holder. The excitation chamber consisted of a ⅛" O.D. stainless steel electrode supported concentrically inside a ¼" I.D. Pyrex tube which was wrapped on the outside with aluminum foil for a length of 3". A Tesla coil was connected to the stainless steel electrode thus providing an R.F. field between the electrode and the grounded aluminum foil. The ion trap consisted of two 20" long stainless steel plates spaced 3/16" apart by strips of Teflon. A D.C. potential was applied between the plates which was of sufficient magnitude to remove all electrically charged species from the effluent gas. The sample holder provided a means of supporting the surface to be treated in a plane perpendicular to the direction of gas flow and at a specific distance from the end of the apparatus.

When nitrogen was passed through this apparatus at a flow rate of 200 cc. per second a sample of polyethylene held 1/16" from the exit tube (a short length of Pyrex tubing fastened to the ion trap) showed a significant *increase* in its hydrophilicity after being treated for 10 seconds. The technique of measuring the angle between the sample surface and the tangent at the point of contact of a drop of water was one method used to detect changes in hydrophilicity.

Example 2

Example 1 was repeated using helium in the system instead of nitrogen. The results were essentially the same.

Example 3

Example 1 was repeated using hydrogen in the system instead of nitrogen. Again the results showed an increase in hydrophilicity.

Example 4

Example 1 was repeated using air instead of nitrogen. In this case the treatment time had to be increased about 70 times in order to get the same level of increase in hydrophilicity.

Example 5

Example 1 was repeated using oxygen instead of nitrogen. The results here were about the same as for *air*.

Example 6

Example 1 was repeated but in this case the sample treated was a piece of stainless steel having a polished surface. After a treatment time of 30 seconds the surface was shown to be more hydrophilic.

Example 7

Example 1 was repeated using a variety of sample materials including polyesters, cellulose acetate, and paper. All of the materials tested showed their surfaces to be more hydrophilic after treatment. However, the treatment time required for a given change varied considerably among the different samples.

The invention has been described in detail with particular reference to preferred embodiments thereof, but it will be understood that variations and modifications can be effected within the spirit and scope of the invention.

I claim:

1. A method for increasing surface hydrophilicity of a normally hydrophobic polymeric material comprising the steps of exciting a gas selected from the group consisting of argon, helium, hydrogen, krypton, neon, xenon, nitrogen, and mixtures thereof with a source of radio frequency radiation, to form activated species thereof, removing substantially all charged particles formed during excitation, and directing said activated species substantially free of charged ions, into contact with the surface of said material to be treated at a location remote from the source of radiation.

2. The method according to claim 1 wherein said step of removing substantially all charged particles includes: passing said activated species through an ion trap prior to directing said stream onto the surface to be treated.

3. An apparatus for treating the surface of a normally hydrophobic polymeric material with an excited gas species to render the surface more hydrophilic comprising a housing having an entrance capable of receiving an excitable gas, radio frequency generation means within the housing near said entrance and adapted to electronically excite the gas received through the entrance to form an active species thereof, the housing provided with an exit through which the excited gas species passes, means for supporting said material in the path of said excited gas species and wherein said housing is further provided with at least two oppositely charged plates between which a gas stream can flow, such plates being located inside said housing between said radio frequency generation means and the exit of said housing and thereby forming an ion trap for removing charged particles from the activated gas species can be directed against a surface to be treated.

References Cited

UNITED STATES PATENTS

3,294,583	12/1966	Fedow-Fedotowsky	204—192
3,309,299	3/1967	Mantell	204—165

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