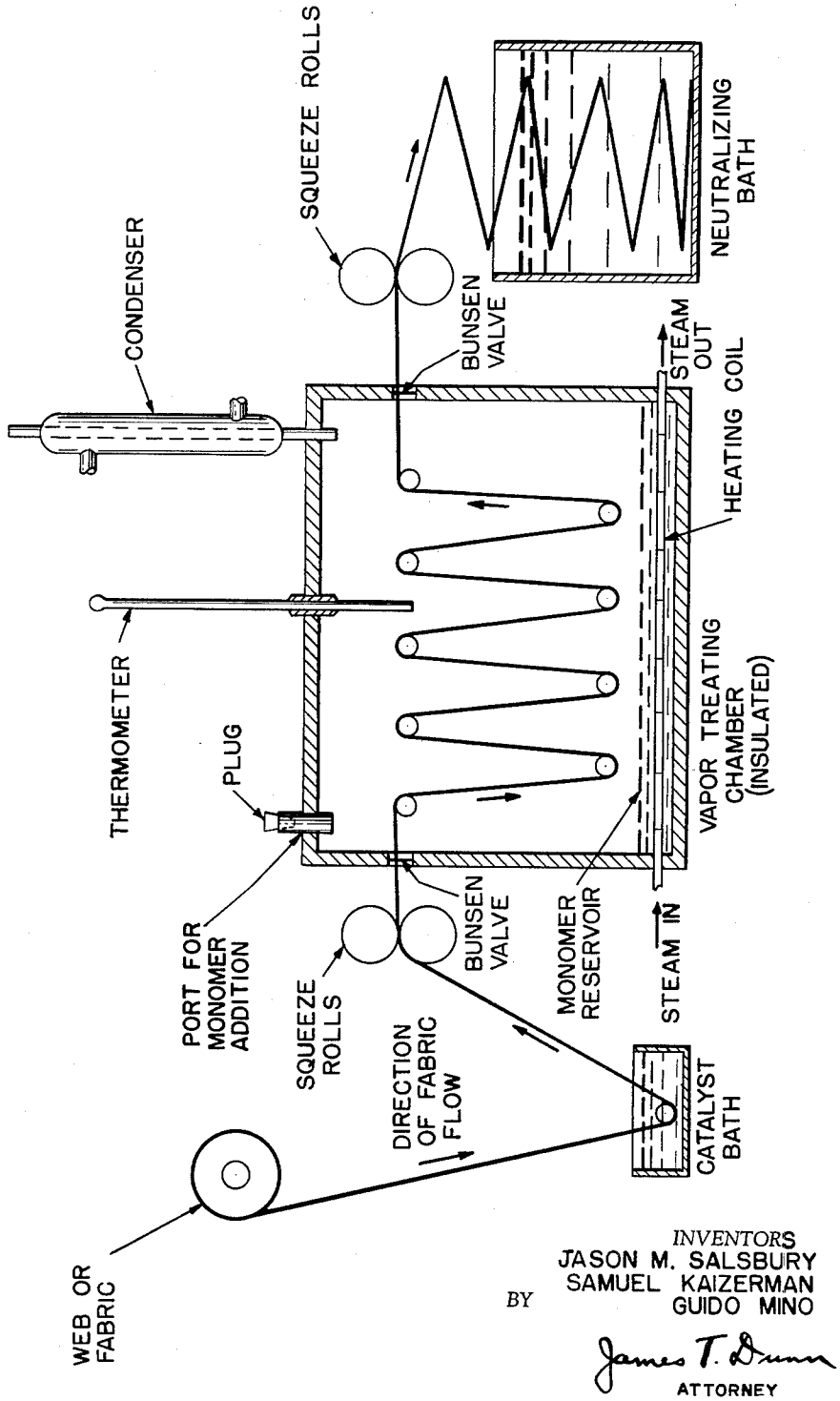
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GRAFT POLYMERIZATION PROCESS

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GRAFT POLYMERIZATION PROCESS

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This invention relates to a process for treating cellulosic materials whereby polymerizable vinyl and/or vinylidene monomers are graft-polymerized onto the cellulosic material in the vapor phase by use of a ceric salt as the oxidizing agent. Still further, this invention relates to the process of treating textile fabrics and paper webs with a polymerizable vinyl and/or vinylidene monomer in the vapor phase in the presence of a ceric salt whereby said monomer is graft-polymerized onto said fabric or web.

One of the objects of the present invention is to graft-polymerize a vinyl or vinylidene monomer onto a cellulosic material by maintaining the monomeric material in the vapor phase and in the presence of a ceric salt. A further object of the present invention is to impart unusual properties to cellulosic materials by the practice of the process of the present invention. These and other objects of the present invention will be discussed in greater detail hereinbelow.

The polymerization in general of olefinic monomers within the fibers of cellulosic materials is known in the prior art but the prior art methods have suffered from a plurality of limitations. The most serious of these limitations resides in the simultaneous polymerization of the monomeric material in the treatment bath, on the surface of the cellulosic material with some small measure of the polymerization taking place within the fibers themselves. This shortcoming results in a waste of the monomeric material, the production of an objectionable layer of polymer on the surface of the cellulosic material, which layer is often difficult if not virtually impossible to remove. The instant invention is a substantial advancement in the art over the known polymerization techniques of the prior art inasmuch as the polymerization can be made to occur substantially entirely within the fibers of the cellulosic material. Additionally, the polymer then deposited on the base is largely grafted to the cellulosic material and becomes an integral part of the cellulosic base material. Still further, there is no wastage of the monomeric material by polymerization in the vapor chamber apart from that taking place in the grafting mechanism on the base material. A further advantage of the present invention resides in the fact that the process can be carried out at a considerably faster rate than the processes of the prior art.

The cellulosic materials which may be used in the practice of the process of the present invention may be in the form of a fiber such as cotton fibers or a fabric either woven or unwoven such as cotton cloth or a matted web such as paper. Still further, the process of the present invention is applicable to films and synthetic fibers which are composed predominantly of cellulosic materials which have been subjected to chemical treatment such as regenerated cellulosic film (cellophane), viscose film, viscose rayon and the like. These cellulosic materials must be sufficiently porous and/or absorbent so as to allow liquids and gases to come into intimate contact with the polymer reducing agent.

The polymerizable vinyl and/or vinylidene monomers which may be used in the practice of the process of the present invention are those containing a polymerizable $CH_2{=}C<$ group having a boiling point not above 150° C. at atmospheric pressure and soluble in water to the extent of at least 0.5% at the temperature of the reaction. It is preferred that the polymerizable monomeric material have a boiling point not appreciably below about 20° C. Among the suitable monomers which may be used in the practice of the process of the present invention are the acrylic compounds such as acrylonitrile, methyl acrylate, ethyl acrylate, propyl acrylate, butyl acrylate, methyl methacrylate, ethyl methacrylate, the vinyl or vinylidene esters and ethers such as vinyl acetate, vinylidene chloride, divinyl ether, vinyl ethyl ether, divinyl sulfide or allyl compounds such as allyl alcohol, allyl acetate and the like. These polymerizable monomers may be used either singly or in combination with one another.

The ceric salts which may be used in the practice of the process of the present invention include ceric nitrate, ceric sulfate, ceric ammonium nitrate, ceric ammonium sulfate, ceric iodate, and the like. Additionally, one may make use of ceric dihexyl sulfosuccinate, ceric dioctyl sulfosuccinate. These ceric salts are preferably dissolved or dispersed in an acidic material, preferably an inorganic acidic material, prior to use on the cellulosic material. The pH of the ceric salt acid medium should be 3.5 or below. The acidic material may be sulfuric acid, perchloric acid, nitric acid, and the like. The concentration of the ceric salt in the catalyst solution may vary from about 1×10^{-4} to about 2×10^{-1} gram-mols per liter. The preferred concentration is between about 1×10^{-3} and 1×10^{-2} gram-mols per liter. These concentrations may also be expressed as 0.0001–0.2 molar and preferably 0.001–0.01 molar. The amount of catalyst solution which is picked up by the material to be treated may vary from 40% to 200% by weight of the material. The preferred pickup is between about 75% and 125% by weight based on the weight of the material.

In practicing the process of the present invention, a cellulosic material such as woven cotton fabric is passed through a catalyst solution comprising a ceric salt dissolved in an acid solution whereby the fabric becomes wetted and impregnated with the catalyst solution. While still in a wetted state, the impregnated web is introduced into the vapor chamber and permitted to pass therethrough by use of a plurality of reverse rollers at a controlled residence time sufficient to enable the monomer vapors present in the chamber to graft-polymerize on the cotton fabric. Thereafter, the web is removed from the vapor chamber and passed through a pair of squeeze rolls in order to remove any excess liquid on the fabric and then dried. In order to control the amount of graft-polymerization taking place on the cotton fabric, one need only control the residence time in the vapor chamber. Thereafter, one may neutralize the treated fabric upon its removal from the vapor chamber by passing the fabric through a neutralizing bath followed by a squeezing and drying operation.

Reference is made to the accompanying drawing which is substantially self-explanatory, particularly in light of the instant disclosure. Reference to said drawing may be made in order to understand more completely the concept of the present invention as set forth in the following examples in which all parts are parts by weight unless otherwise indicated. These examples are set forth primarily for the purpose of illustration and any specific enumeration of detail contained therein should not be interpreted as a limitation on the case except as is indicated in the accompanying claims.

Example 1

A cotton fabric web emanating from the source roll is passed through the catalyst bath containing 0.01 molar solution of ceric ammonium sulfate in a 0.1 molar solution of sulfric acid. The wetted web is then passed through

the squeeze rolls, to give a wet pickup of approximately 110%, and then through the Bunsen valve into the vapor treating chamber filled with the vapor from a boiling acrylonitrile-water azeotrope. The rate of movement of the wetted web through the vapor treating chamber is such as to give the web a residence time in the chamber of 2 minutes. The fabric is removed from the chamber, squeezed through the squeeze rolls, passed through the neutralizing bath to remove residual acrylonitrile, acid and ceric salt and is then dried. The weight increase of the fabric due to polymer deposition is 21.7%. The fabric thus treated showed outstanding resistance to degradation by microorganisms; showed no strength loss after 6 weeks burial in soil whereas untreated fabric buried in the same soil disintegration completely in less than 2 weeks.

Example 2

A web of regenerated cellulosic film is thoroughly washed with water to remove the plasticizer. The film is soaked for 1 minute in a 0.1 molar solution of ceric ammonium nitrate in 0.1 molar solution of nitric acid. The web is then passed through the squeeze rolls and into the vapor treating chamber filled with the vapor from a boiling methyl acrylate-water azeotrope. The residence time in the chamber is approximately 1 minute. Upon removal from the chamber, the film is washed and dried. The weight increase due to polymer deposition is found to be 52.8%. The treated film is more flexible than the untreated, unplasticized material. The polymer deposit is completely resistant to extraction by a wide variety of solvents.

It has been indicated hereinabove that the amount of polymer deposition on the cellulosic material may be controlled by varying the residence time in the vapor chamber. This residence time can be varied over a fairly substantial range. Periods of time as short as 10 seconds may be used or the residence time can be controlled so as to maintain the cellulosic material in the vapor chamber for periods of 1 hour or even 2 hours or more. When the residence time is too extended, the process may become cumbersome unless there is a particularly desirable reason for maintaining the residence time at more than 2 hours. For most practical purposes, residence times of between about 1 minute and 15 minutes should be sufficient.

It should be noted in the above examples that use is made of a monomer-water azeotrope. This is not imperative inasmuch as the monomer could be utilized alone without the benefit of any added water. It is preferred, however, particularly for those monomers having a boiling point about 100° C., to use a small amount of water with the monomer so as to provide a lower boiling mixture. The amount of water that will be added may be varied between about 10% and 25% by weight based on a total weight of monomer and water.

The temperature of the vapor in the vapor chamber may be controlled by heating at the base of the chamber so as to put the monomer or monomer-water mixture in the vapor phase at a temperature between about 20° C. and 150° C. Preferably, one would operate between about 30° C. and 110° C. When using the monomer-water azeotrope, one can increase the amount of vapor of monomer in the chamber at temperatures below the normal boiling point of the monomer and as a consequence, it is sometimes advantageous to employ such a mixture.

The amount of monomer polymerized on the cellulosic base material may be varied by controlling any one or all of (1) the amount of catalyst pickup, (2) the temperature in the vapor chamber and (3) the residence time of the material in the chamber.

We claim:

1. A process comprising continuously contacting and wetting a cellulosic material with an acidic dispersion of a ceric salt, passing said wetted material through an atmosphere of a polymerizable monomer having a polymerizable $CH_2{=}C<$ group, wherein said monomer has a boiling point between about 20° C. and 150° C. and is soluble in water to at least 0.5%, in the vapor state, at a temperature elevated sufficiently to maintain said monomer in the vapor phase and for a period of time sufficient to graft-polymerize said monomer on said material wherein said process is carried out at substantially atmospheric pressure.

2. A process comprising continuously contacting and wetting cotton with an acidic dispersion of a ceric salt, passing said wetted cotton through an atmosphere of a polymerizable monomer having a polymerizable

$$CH_2{=}C<$$

group, wherein said monomer has a boiling point between about 20° C. and 150° C. and is soluble in water to at least 0.5%, in the vapor state, at a temperature elevated sufficiently to maintain said monomer in the vapor phase and for a period of time sufficient to graft-polymerize said monomer on said cotton wherein said process is carried out at substantially atmospheric pressure.

3. A process comprising continuously contacting and wetting cellulosic paper with an acidic dispersion of a ceric salt, passing said wetted cellulosic paper through an atmosphere of a polymerizable monomer having a polymerizable $CH_2{=}C<$ group, wherein said monomer has a boiling point between about 20° C. and 150° C. and is soluble in water to at least 0.5%, in the vapor state, at a temperature elevated sufficiently to maintain said monomer in the vapor phase and for a period of time sufficient to graft-polymerize said monomer on said cellulosic paper wherein said process is carried out at substantially atmospheric pressure.

4. A process comprising continuously contacting and wetting regenerated cellulosic film with an acidic dispersion of a ceric salt, passing said wetted regenerated cellulosic film through an atmosphere of a polymerizable monomer having a polymerizable $CH_2{=}C<$ group, wherein said monomer has a boiling point between about 20° C. and 150° C. and is soluble in water to at least 0.5%, in the vapor state, at a temperature elevated sufficiently to maintain said monomer in the vapor phase and for a period of time sufficient to graft-polymerize said monomer on said regenerated cellulosic film wherein said process is carried out at substantially atmospheric pressure.

5. A process comprising continuously contacting and wetting rayon with an acidic dispersion of a ceric salt, passing said wetted rayon through an atmosphere of a polymerizable monomer having a polymerizable

$$CH_2{=}C<$$

group, wherein said monomer has a boiling point between about 20° C. and 150° C. and is soluble in water to at least 0.5%, in the vapor state, at a temperature elevated sufficiently to maintain said monomer in the vapor phase and for a period of time sufficient to graft-polymerize said monomer on said rayon wherein said process is carried out at substantially atmospheric pressure.

6. A process comprising continuously contacting and wetting a cellulose material with an acidic dispersion of a ceric salt, passing said wetted material through an atmosphere of acrylonitrile, in the vapor state, at a temperature elevated sufficiently to maintain said acrylonitrile in the vapor phase and for a period of time sufficient to graft-polymerize said acrylonitrile on said cellulosic material wherein said process is carried out at substantially atmospheric pressure.

7. A process comprising continuously contacting and wetting a cellulosic material with an acidic dispersion of a ceric salt, passing said wetted material through an atmosphere of methyl acrylate, in the vapor state, at a temperature elevated sufficiently to maintain said methyl acrylate in the vapor phase and for a period of time sufficient to graft-polymerize said methyl acrylate on said

cellulosic material wherein said process is carried out at substantially atmospheric pressure.

8. A process comprising continuously contacting and wetting a cellulosic material with an acidic disperson of a ceric salt, passing said wetted material through an atmosphere of ethyl acrylate, in the vapor state, at a temperature elevated sufficiently to maintain said ethyl acrylate in the vapor phase and for a period of time sufficient to graft-polymerize said ethyl acrylate on said cellulosic material wherein said process is carried out at substantially atmospheric pressure.

9. A process comprising continuously contacting and wetting cotton with an acidic dispersion of a ceric salt, passing said wetted material through an atmosphere of acrylonitrile, in the vapor state, at a temperature elevated sufficiently to maintain said acrylonitrile in the vapor phase and for a period of time sufficient to graft-polymerize said acrylonitrile on said cotton wherein said process is carried out at substantially atmospheric pressure.

10. A process comprising continuously contacting and wetting cellulosic paper with an acidic dispersion of a ceric salt, passing said wetted material through an atmosphere of methyl acrylate, in the vapor state, at a temperature elevated sufficiently to maintain said methyl acrylate in the vapor phase and for a period of time sufficient to graft-polymerize said methyl acrylate on said cellulosic paper wherein said process is carried out at substantially atmospheric pressure.

11. A process comprising continuously contacting and wetting cellulosic paper with an acidic dispersion of a ceric salt, passing said wetted material through an atmosphere of ethyl acrylate, in the vapor state, at a temperature elevated sufficiently to maintain said ethyl acrylate in the vapor phase and for a period of time sufficient to graft-polymerize said ethyl acrylate on said cellulosic paper wherein said process is carried out at substantially atmospheric pressure.

12. A process comprising continuously contacting and wetting regenerated cellulosic film with an acidic dispersion of a ceric salt, passing said wetted material through an atmosphere of acrylonitrile, in the vapor state, at a temperature elevated sufficiently to maintain said acrylonitrile in the vapor phase and for a period of time sufficient to graft-polymerize said acrylonitrile on said regenerated cellulosic film wherein said process is carried out at substantially atmospheric pressure.

13. A process comprising continuously contacting and wetting regenerated cellulosic film with an acidic dispersion of a ceric salt, passing said wetted material through an atmosphere of ethyl acrylate, in the vapor state, at a temperature elevated sufficiently to maintain said ethyl acrylate in the vapor phase and for a period of time sufficient to graft-polymerize said ethyl acrylate on said regenerated cellulosic film wherein said process is carried out at substantially atmospheric pressure.

14. A process comprising continuously contacting and wetted rayon with an acidic dispersion of a ceric salt, passing said wetted material through an atmosphere of acrylonitrile, in the vapor state, at a temperature elevated sufficiently to maintain said acrylonitrile in the vapor phase and for a period of time sufficient to graft-polymerize said acrylonitrile on said rayon wherein said process is carried out at substantially atmospheric pressure.

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