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MANUFACTURE OF LAMINATED WEBS OF CELLULOSE ESTER FIBERS

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Various processes are known, by means of which cellulose fibers can be converted into cellulose ester or ether fibers while maintaining their structure. The esterification or etherification of laminated cellulose strips, sheets or layers as well as the conversion of esterified cellulose fibers into the laminated form has also already been described.

Whereas previously formed cellulose layers such as paper strips when subsequently suitably esterified while maintaining their structure, always show good electrical properties and a low capacity for absorbing water after the esterification, strips or webs of cellulose ester fibers whose formation has only been effected after the esterification by the usual process of milling, making into a paste and filtering, characteristically show distinctly worse electrical properties and lower resistance to water.

As the electrical properties, for example the insulating power and the hygroscopic nature of the cellulose ester fibers manufactured while maintaining their structure depend in the first place on the degree of esterification, it is probable that the milling of the esterified cellulose fibers absolutely necessary for the adhering layer formation, exposes new surfaces which are less esterified and consequently show less favorable properties.

According to the present invention it has now been found that fibrous cellulose ester strips, sheets, layers or webs of any kind can be manufactured which have extraordinarily good electrical properties and a very high stability to water, if the milling takes place either before the esterification, during the esterification or even after the actual esterification provided that in the latter case it takes place still in the esterification mixture itself and the formation of layers is carried out subsequently with the avoidance of any injury to the fibres.

The lamination or formation of sheets can take place as desired directly from the esterification mixture, possibly after the rendering inactive of the esterification catalyst or catalysts or after the dilution of the esterification mixture with lower fatty acids, or organic solvents, which do not tend to dissolve the esterified fibers, or even not until after the separation of the fibers from the acetylation mixtures and subsequent washing out but preferably still in the moist swollen condition, that is before drying.

The laminated strips of cellulose ester fibers thus manufactured are not inferior in electrical properties to the laminated strips of cellulose ester fibers obtained by the esterification of preformed laminated cellulose strips but even show just as good or even better electrical properties as for example those shown by fibrous cellulose ester yarns or fabrics manufactured from cotton yarns or fabrics maintaining their structure.

The newly invented method of working for the manufacture of laminated strips of cellulose ester fibers brings with it in an unexpected manner quite a series of technical advances.

It is obvious that the acetylation of loose fibers is technically easier to carry out than the esterification of completed cellulose strips, which, particularly in the moist condition, are relatively easily damaged and can therefore only be worked up in complicated apparatus. The use of simpler apparatus in the esterification of loose fibers means, owing to the extraordinary activity of the acetylation mixture, a technical advance not to be underestimated.

The swelling which always occurs during esterification brings further advantages with it. It is known that the formation of cohesive layers of sufficient strength from cellulose is only possible after a certain swelling of the cellulose fibers, for which reason, for example in the case of paper manufacture, milling in the hollander or a similar device cannot be avoided. The swelling which takes place automatically during the esterification simplifies the later formation of cohesive layers so that the duration of the milling can be considerably shortened. As the swelling increases with increasing esterification it is possible by suitable correlation of the milling and the degree of esterification, to manufacture strips of cellulose ester fibers of less strongly disintegrated, i. e. less strongly mechanically attacked, cellulose fibers and to manufacture therefrom strips of special strength.

The esterification of the cellulose fibers with maintenance of their fibrous structure can be carried out according to known processes with lower and higher fatty acid derivatives to any degree of esterification desired in the presence or absence of organic solvents in which the resulting cellulose esters are insoluble. As catalysts the known esterification accelerators may be used preferably those which do not form any stable compounds with the cellulose during the esterification and during later washing out, such as for example the known acid reacting catalysts, such as the hydrogen halide acids, perchloric acid, halogenated carboxylic acids, organic sulphonic acids etc. while the polyvalent mineral acids which themselves form cellulose esters such as for example free sulphuric or phosphoric acid are less suitable; further the halogens, or salt-like catalysts, such as zinc chloride, tin chloride, ferric chloride, copper sulphate or perchlorates can be used. Naturally mixtures of all the usable catalysts of the most varied kinds may be used.

The formation of layers of fibrous cellulose ester can take place in known manner on sieves or filters, that is for example by means of the usual paper pulp devices for the manufacture of paper strips, long sieves, drum filters etc. If the formation of layers takes place directly from the esterification mixture or after the dilution thereof, it is naturally advisable owing to the chemical attack on the apparatus to use a closed apparatus of as simple as possible a nature.

In case it is desired to produce paper sheets etc. from water suspensions of esterified fibers, the procedure is the following:

After the acetylation the fibrous cellulosic material is hydroextracted, washed in water and finally homogeneously suspended in water. From this suspension sheets, strips, layers of paper and cardboard etc. can be formed in the well known manners.

Sheet papers and cardboards formed from this suspension of esterified cellulosic materials in water have a tensile strength which is below the usual one found with such materials. If the fibers have been washed absolutely free from the acetylation mixture the tensile strength is low; if more or less acetylation mixture is left in the fiber and the suspension and sheet formation is carried out quickly the tensile strength of the resulting paper or strips etc. is fairly good, but still lower than the values generally found with these materials.

It has now been found that this tensile strength can be greatly improved by a simple additional process consisting of an aftertreatment with aliphatic carboxylic acid in vapor or liquid form, such as e. g. acetic acid. The sheet paper, strip, cardboard etc. passes through a bath of glacial acetic acid or acetic acid diluted with water. The acid is afterwards completely recovered by evaporation and the paper etc. has then greatly improved in tensile strength.

The subsequent further treatment of the layers to form the strips of cellulose ester capable of being handled commercially takes place according to known methods taking into consideration the special chemical composition and physical properties of the material. In this connection it should be mentioned, that in many cases it is advisable to subject the cellulose ester strips to a treatment with steam under pressure, which per se is likewise conventional.

Special care must be used in the selection of possible additional substances, such as adhesives, fillers or softening substances. As cellulose esters are capable of swelling or are soluble in certain organic solvents, the strips of cellulose esters can have their physical form altered by the action of such solutions and swelling agents. All these details can naturally be varied to an extraordinary extent according to the intended use, and do not depend directly on the essence of the invention, which is the careful manufacture of laminated strips of cellulose ester fibers from esterified fibers. Naturally strips of the most varied thickness of layer, from the thinnest tissue paper to the thickest cardboard can be manufactured by this process. The special chemical composition of such strips of cellulose ester fibers also makes possible the manufacture of a new type of fabric such as translucent masses (parchment paper), as well as the manufacture of specially shaped bodies in which a plurality of layers are superimposed and may if desired also be bound by fillers.

The fact that the layers of cellulose ester fibers are considerably more stable to rise of temperature than are strips of unesterified cellulose is particularly advantageous.

Further advantages result also from the fact that the strips of cellulose ester fibers are resistant to micro-organisms, i. e. they are resistant to putrefying bacteria, molds, fungi, etc. and are not devoured by quite a large number of insects even for example by termites.

Such strips of cellulose ester fibers can therefore be used, not only as electrical insulation material, but also as packing material for foodstuffs, for bandages, for wall paper insensitive to dampness, or in the form of paste board even directly as building material, as well as for a whole series of other technical purposes.

The following examples serve to illustrate the practical carrying out of the process described, without limiting it in any way.

Example 1

Bleached linters are previously dried and carefully milled in a closed apparatus corresponding to the usual hollander at a somewhat raised constant temperature in an acetylation mixture suitable for the manufacture of slightly acetylated cellulose fibers, consisting of acetic anhydride, anhydrous acetic acid and zinc chloride as catalyst until the esterification has proceeded completely to a stage corresponding to cellulose monoacetate. Then the acetylation mixture is diluted with anhydrous acetic acid and the loose fibers worked up in a known manner to a strip of cellulose acetate fibers for example by means of an evacuable perforated roller. The fiber strip obtained is freed as completely as possible from adhering acetylation mixture by warming in a current of air, thoroughly washed and dried.

Other things being equal the fibers swell more or less strongly during the acetylation depending on the intensity of the milling, so that the formation of the fibrous strip on the rotating roller takes place more easily or with more difficulty. If milling is effected energetically during the whole of the acetylation a completely homogeneous pulp of fibers results, which can no longer filter very well and is therefore worked up more easily by pouring into water and molding to a paper strip from aqueous suspension.

If with every method of working up care is taken that the cellulose monoacetate fibers are not subsequently damaged, then the cellulose ester strips resulting show good mechanical and electrical properties, namely a high tearing strength, an outstanding power of insulation, a small power factor, and a small dielectric constant, further a very good resistance to water. The values obtained are just as high as those of a strip of paper, manufactured from linters and then esterified to the monoacetate stage, the structure being maintained completely.

This result is astonishing as hitherto it has not been possible, in spite of numerous experiments, to manufacture cellulose ester strips, from fibers acetylated in the loose form, with just as good mechanical and electrical properties as the corresponding cellulose acetate fiber strips which have been obtained by the acetylation of completed papers.

If linters for example under exactly the same conditions are converted into cellulose monoacetate and milled in aqueous suspension for the purpose of paper manufacture, then the insulating properties diminish with the increasing degree of milling to a fraction of the original value. If the insulating power of linters for example esterified to the monoacetate stage amounts to approximately 1,000,000 megohms per gram of fibrous material at 500 volts direct current, 80% relative atmospheric humidity and 25° C., then paper manufactured therefrom by milling in water and molding to a strip of cellulose ester fibers shows an insulation power which diminishes depending on the degree of milling. After half an hour's milling of the fibers in the hollander the paper manufactured therefrom still shows for example a tenth part of the original insulation resistance, namely approximately 100,000 megohms per gram; after milling for an hour only a hundredth part namely approximately 10,000 megohms per gram, after two hours milling only a five hundredth part, namely only approximately 2,000 megohms per gram fibrous material.

By way of comparison a fibrous cellulose strip manufactured from ground linters when subsequently esterified to the monoacetate stage under the same conditions likewise shows an insulation power of approximately 1,000,000 megohms per gram.

In the same way the stability to water of acetylated cellulose fiber is made worse by the milling, i. e. cellulose acetate fibers become more and more hygroscopic when ground in an aqueous medium.

Example 2

Purified cotton spinning waste is milled in 95% acetic acid in a pin mill until a homogeneous fibrous pulp results, centrifuged and esterified in an acetylating mixture of acetic anhydride, acetic acid, and an organic liquid which prevents the solution of the resulting higher cellulose acetates, such as low boiling paraffin hydrocarbons (benzine), aromatic hydrocarbons (benzene, toluene, solvent naphtha etc.), halogenated hydrocarbons (carbon tetrachloride, chlorobenzene, etc.) and perchloric acid as a catalyst, the esterification is carried out up to an acid content of 60% that is almost until the triacetate stage, and after the addition of a quantity of sodium acetate corresponding to the perchloric acid and an excess of the organic liquid used, molded on a closed round or long sieve machine to a highly esterified cellulose acetate strip. The resulting cellulose ester strip is freed as far as possible from adhering liquid by warming, dried, washed and calendered on hot rollers. The insulating power of the highly esterified cellulose acetate fiber strip under the same conditions of measurement as those described in Example 1 shows an insulation value of over 50 million megohms per gram.

Instead of molding the cellulose acetate strips from the acetylation mixture itself, the highly acetylated cellulose fibers can also be freed thoroughly from excess acetylation mixture, suspended in water, thoroughly washed and the subsequent layer formation carried out from the aqueous suspension. The dried highly esterified cellulose acetate fiber strip can if necessary be subjected to a further treatment with water vapor under pressure, the insulating nower and resistance to water being somewhat further improved.

Example 3

Disintegrated sodium cellulose obtained by treatment of wood cellulose with aqueous alkaline solutions is esterified to the stage corresponding to cellulose monoacetate in the known manner with gentle stirring or circulation of the bath in an acetylation mixture of acetic anhydride, glacial acetic acid and 1.5-naphthalene disulphonic acid at raised temperature, the esterification mixture cooled and the monoacetate fibers in the mixture are milled in a ball-mill until a sample gives a perfect layer formation, the 1.5-naphthalene disulphonic acid converted into the sodium salt by the addition of sodium acetate diluted with acetic acid, and molded in a closed round sieve machine to a cellulose monoacetate fiber strip, washed and dried. During the relatively short milling period the acetic acid content of the fibers rises only slightly.

The insulating power of a cellulose monoacetate fiber strip amounts to values of over 1/4 million megohms per gram, whereas paper prepared by the subsequent milling in aqueous solution of sodium cellulose fibers which have been acetylated to the stage corresponding to monoacetate while retaining their structure only shows an insulating power of approximately 2,000 megohms per gram, that is not even a hundredth part of that of the cellulose acetate fiber strip manufactured according to the process of this invention.

If the esterification is carried beyond the monoacetate stage, for example to an acetic acid content of 36–40%, then the cellulose acetate fiber strips show a parchment paper like character.

Instead of the cotton or sodium celluloses mentioned in Examples 1–3, naturally other fibers consisting of cellulose or cellulose containing fibers can be used as the starting material, such as for example other types of cellulose, wood shavings, bast fibers as well as linen, hemp (manila hemp), ramie, as well as old paper or rags which consist of cellulose fibers or even fibers of regenerated cellulose, such as artificial silk spinnerette waste from viscous or cuprammonium silk etc.

Obviously instead of the acetic acid ester given in the examples other individual or mixed cellulose ester fibers manufactured while maintaining the structure such as fibers of cellulose propionate, -butyrate, -acetobutyrate, -laurate, -acetostearate etc. can be molded to cellulose ester strips according to the present process.

What we claim is:

1. In a process for the manufacture of sheets of cellulose fibers esterified with a lower fatty acid while maintaining the original structure of the fibers, which sheets are characterized by dielectric properties and possess the mechanical properties of paper and cardboard, the steps of milling loose cellulose fibers in a fatty acid medium containing a lower fatty acid whereby esterification and concomitant swelling of the fibers take place, and transforming the resultant fibers into sheet form while the fibers are still in the swollen state due to the esterification and while they still contain a small proportion of the fatty acid medium.

2. In a process for the manufacture of sheets of cellulose fibers esterified with a lower fatty acid while maintaining the original structure of the fibers, which sheets are characterized by dielectric properties and possess the mechanical

properties of paper and cardboard, the steps of milling loose cellulose fibers in a fatty acid medium containing a lower fatty acid, the corresponding acid anhydride and an esterification catalyst whereby esterification and concomitant swelling of the fibers take place, and transforming the resultant fibers into sheet form while the fibers are still in the swollen state due to the esterification and while they still contain a small proportion of the fatty acid medium.

3. In a process for the manufacture of sheets of cellulose fibers esterified with acetic acid while maintaining the original structure of the fibers, which sheets are characterized by dielectric properties and possess the mechanical properties of paper and cardboard, the steps of milling loose cellulose fibers in a fatty acid medium containing acetic acid whereby esterification and concomitant swelling of the fibers take place, and transforming the resultant fibers into sheet form while the fibers are still in the swollen state due to the esterification and while they still contain a small proportion of the fatty acid medium.

4. In a process for the manufacture of sheets of cellulose fibers esterified with acetic acid while maintaining the original structure of the fibers, which sheets are characterized by dielectric properties and possess the mechanical properties of paper and cardboard, the steps of milling loose cellulose fibers in a fatty acid medium containing acetic acid, acetic anhydride and an esterification catalyst whereby esterification and concomitant swelling of the fibers take place, and transforming the resultant fibers into sheet form while the fibers are still in the swollen state due to the esterification and while they still contain a small proportion of the fatty acid medium.

5. In a process for the manufacture of sheets of cellulose fibers esterified with acetic acid while maintaining the original structure of the fibers, which sheets are characterized by dielectric properties and possess the mechanical properties of paper and cardboard, the steps of milling loose cellulose fibers in a fatty acid medium containing acetic acid whereby esterification and concomitant swelling of the fibers take place, removing the esterified fibers from the said medium and transforming the resultant fibers into sheet form while the fibers are still in the swollen state due to the esterification and while they still contain a small proportion of the fatty acid medium.

6. In a process for the manufacture of sheets of cellulose fibers esterified with a lower fatty acid while maintaining the original structure of the fibers, which sheets are characterized by dielectric properties and possess the mechanical properties of paper and cardboard, the steps of milling loose cellulose fibers in a fatty acid medium containing a lower fatty acid whereby esterification and concomitant swelling of the fibers take place, transforming the resultant fibers into sheet form while the fibers are still in the swollen state due to the esterification and while they still contain a small proportion of the fatty acid medium, and finally subjecting the resultant sheets to an aftertreatment with the said lower fatty acid.

7. In a process for the manufacture of sheets of cellulose fibers esterified with acetic acid while maintaining the original structure of the fibers, which sheets are characterized by dielectric properties and possess the mechanical properties of paper and cardboard, the steps of milling loose cellulose fibers in a fatty acid medium containing acetic acid whereby esterification and concomitant swelling of the fibers take place, transforming the resultant fibers into sheet form while the fibers are still in the swollen state due to the esterification and while they still contain a small proportion of the fatty acid medium, and finally subjecting the resultant sheets to an aftertreatment with acetic acid.

8. In a process for the manufacture of sheets of cellulose fibers esterified with a lower fatty acid while maintaining the original structure of the fibers, which sheets are characterized by dielectric properties and possess the mechanical properties of paper and cardboard, the step of transforming the fibers into sheet form while the fibers are in a swollen state resulting from an antecedent esterification thereof by a fatty acid medium containing a lower fatty acid and while the fibers still contain a small proportion of the said medium.

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