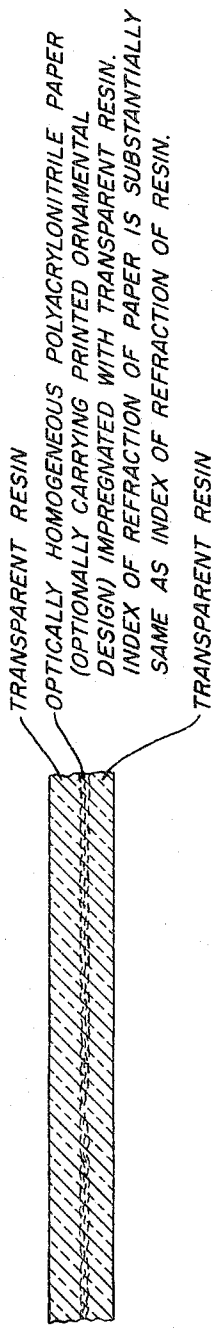
Aug. 2, 1966 J. K. MAGRANE ETAL 3,264,170

POLYACRYLONITRILE PAPER AND METHODS FOR THE MANUFACTURE THEREOF

Filed Feb. 1, 1963



INVENTORS.
JOHN K. MAGRANE
WALTER F. REYNOLDS, JR.
DAVID H. RAKOWITZ

BY

ATTORNEY

United States Patent Office 3,264,170 Patented August 2, 1966

3,264,170

POLYACRYLONITRILE PAPER AND METHODS FOR THE MANUFACTURE THEREOF

John K. Magrane and Walter F. Reynolds, Jr., Stamford, and David H. Rakowitz, Cos Cob, Conn., assignors to American Cyanamid Company, Stamford, Conn., a corporation of Maine

Filed Feb. 1, 1963, Ser. No. 255,476
7 Claims. (Cl. 162—157)

The present invention relates to a continuous method for the manufacture of polyacrylonitrile paper which has high tensile strength and which is substantially optically homogeneous. The invention includes the paper produced by the method, and resinous structures containing the paper.

Polyacrylonitrile paper is commercially manufactured by a continuous process which comprises chopping wet-spun, wet-gel polyacrylonitrile filaments to convenient paper-making length, refining the filaments until they are well fibrillated, sheeting the filaments while still in wet-gel state to form an endless water-laid web, and heating the web to a temperature above about 150° F. by passing the web over a series of heated rolls to dry the web and to heat-bond the fibrils together. Obviously, the temperature of the rolls is controlled so that the paper is not carried above the decomposition point of the polymer of which it is composed.

The resulting paper is sufficiently strong for general commercial purposes.

However, the paper is not optically homogeneous. When immersed in a liquid having the same index of refraction as the polymer of which it is composed, the paper does not become invisible. Instead, it appears as a cloudy, blotchy, or hazy stratum suspended in the liquid. Appearance of this stratum is evidence that collapse of the gel structure during drying is not uniform or complete.

Paper manufactured by drying the wet web at temperatures below 150° F. is optically homogeneous because substantially no collapse of the gel structure occurs at these temperatures and the resulting paper is therefore uniform as to the structure of the fibers. The paper, however, is very weak and is therefore not suited for general commercial use.

A demand has arisen for polyacrylonitrile paper which is both strong and optically homogeneous. It is desired to use such paper in the manufacture of ornamental, substantially transparent sheet material by imprinting an ornamental design upon such paper, impregnating and coating the paper with a transparent thermosetting synthetic resin having substantially the same index of refraction as the polymers or polymer composition of which the paper is composed, and thermosetting the resin so as to form a sheet of plastic which contains the paper. Up to the present, however, polyacrylonitrile paper has proved either too weak or insufficiently homogeneous from the optical point of view to render it satisfactory for this purpose.

In the manufacture of polyacrylonitrile paper, no significant shrinkage of the web occurs during the first part of the drying step (i.e., while its content of free and combined water is being decreased from an initial value of 100% by weight to a value of about 40%). Extensive shrinkage occurs, however, during the terminal part of the drying, and during the heat-bonding of the fibers, i.e. while the web is drying at a temperature in excess of 150° F. from a water content of roughly 40% by weight to the point where the paper is apparently dry and the gel structure of the fibers has substantially completely collapsed. Normal shrinkage of polyacrylonitrile paper during this terminal drying step is in the range of 10% to 20% in each dimension.

The discovery has now been made that polyacrylonitrile paper which is both strong and optically homogeneous is obtained by continuously maintaining the web in an atmosphere of supra-normal relative humidity during this terminal drying step.

It is the continuity of the condition of supra-normal relative humidity which is critical, and paper of the desired optical homogeneity is not produced when maintenance of supra-normal relative humidity is interrupted during the drying step. Such interruption occurs, for example, when a web passes from one drying roll to another in the drying section of a paper-making machine and is thereby exposed to normal (unhumidified) atmospheric air. By means of this discovery, we having produced optically homogeneous polyacrylonitrile paper which has a tensile strength sufficiently high so that this paper (particularly at low basis weights) can be used in web-fed continuous machines for the manufacture of transparent resinous structure.

The structure referred to above is illustrated in FIG. 1, which is a schematic vertical section of transparent sheet material containing a paper sheet produced in accordance with the process of the present invention. The sheet material consists essentially of the paper sheet (which if desired may carry an ornamental or printed design) impregnated with and coated on both sides with a transparent resin, the index of refraction of the resin and of the paper being substantially the same.

Evidently the effect of supra-normal relative humidity is to retard the rate at which water evaporates from the paper and thus to retard the rate at which the gel structure of the paper collapses. The result of this is formation of polymeric structure is which the gel structure has uniformly and completely collapsed, so that it does not contain vacuoles of visible size.

We have further found that production of optically homogeneous paper can be achieved in shorter time by maintaining the paper under dimensional restraint as it dries, so that the amount of shrinkage which the paper undergoes as it dries is decreased.

In practice best results are obtained when the web is dried in an atmosphere of 90%–100% relative humidity and when the web is under as tight dimensional restraint as is practical, so that shrinkage of the web during drying is at a minimum.

Laboratory tests have shown that paper of substantially as good optical homogeneity is obtained when the drying is performed in an atmosphere of moderate (20%) relative humidity as in an atmosphere which approaches saturation. The invention thus does not primarily reside in the elevation of the humidity of the drying atmosphere to any specific value. The invention likewise does not primarily depend upon the particular way in which an atmosphere of supra-normal humidity is maintained about the wet web as it dries, and there are several methods which may be employed for the purpose.

If desired, the web may be dried by passage through a continuous controlled humidity-temperature drier. The drier is advantageously set to maintain a temperature in the range of 200°–250° F. An absolute humidity of 15 to 40 g. of water vapor per 100 grams of dry air in the drier (roughly corresponding to a relative humidity of 25%–50%) has proved satisfactory. Normal air (air having a relative humidity of 50% at 70° F.) when heated to the temperature of the drier has a relative humidity of about 3% to 6%.

In commercial practice it has been found practical to perform the drying step in the drying section of a standard paper-making machine, when the web was maintained between felts from the point where the water content of the web is 40%–35% by weight to the point at which collapse of the gel of the web was substantially complete.

The felts were maintained under tight tension to minimize shrinkage of the web as it dried and to prevent access of atmospheric air to the web as it passed from roll to roll. Brief exposure of the web to atmospheric air during drying (such as occurs when the web passes the end-point of one pair of felts and the starting point of another pair of felts) is not usually significantly detrimental.

If desired, the web may be dried over a single drum drier as, for example, a Yankee drier. If this type of drier is used, the web may be run in direct contact with the drum of the drier as is customary. However, a felt should be run along with and over the web, by means of which the web is maintained in an atmosphere of supra-normal humidity as it dries. The drying capacity of a Yankee drier is such that the web is dry when it leaves the drum.

The porosity of the felts coupled with their density (i.e., their close pore structure) permits the maintenance of an atmosphere of supra-normal relative humidity about the fibers during at least a preponderant part of the drying because the wet web steadily evolves water vapor as it dries, and the dense porous nature of the felts prevents substantial access of atmospheric air to the web. Atmospheric air at the drying temperatures of 200°–250° F. has a very low relative humidity and it is the quick drying effect of this very dry air which causes the development of paper which lacks optical homogeneity.

The felts referred to are preferably made of wool, and are about ⅛" thick. Any membrane material which will permit evolved water vapor to pass through it and which will protect the web from access of atmospheric (dry) air would be satisfactory. Woolen felts have a special advantage in that they have a rough surface and resist lateral compression. The rough surface of the felts uniformly engages the surface of the web which is being dried and the resistance of the felts to lateral compression inhibits, often by 50%, the shrinkage that would otherwise take place.

In the specification and claims the term "polyacrylonitrile paper-making filaments" includes paper-making filaments composed solely of polyacrylonitrile and paper-making filaments composed of a co- or interpolymer of acrylonitrile with a minor amount of one or more ethylenically unsaturated monomers copolymerizable therewith, as is shown in Wooding et al. U.S. Patent No. 2,810,646; Anderson et al. U.S. Patent No. 3,047,455; and in the patents referred to therein. The term further includes blends or solid solutions of a major amount of one or more than one of the foregoing polymers with a minor amount of one or more than one polymer compatible therewith.

The step of drying a web at elevated temperature in an "atmosphere of supra-normal relative humidity" designates a drying performed in an atmosphere which has a relative humidity in excess of the relative humidity which air at 70° F. and 50% relative humidity has when heated to that temperature.

The invention will be further illustrated by reference to the examples. These examples constitute embodiments of the invention and are not to be regarded as limitations thereon.

Example 1

The following illustrates the necessity of maintaining an atmosphere of supra-normal relative humidity about a polyacrylonitrile web for the production of high tensile strength optically homogeneous polyacrylonitrile paper.

An aqueous paper-making suspension composed of ½" long 3-denier, wet-spun, wet-gel polyacrylonitrile filaments of 90:10 polyacrylonitrile:methyl methacrylate copolymer is refined at pH 7 until the filaments are well fibrillated, that is, until they have fibrillated to about the extent shown in FIG. 2 of U.S. Patent No. 2,810,646.

A wet web is prepared by flowing a part of the suspension at a consistency of 0.6% over a paper-maker's screen. The web is pressed on a felt between rolls to a moisture content estimated at 70%.

A part of this web is air-dried in an atmosphere having a temperature of 20° C. and a relative humidity of 50%. The paper thus obtained has a basis weight of 52.6 lbs. per 25" x 40"/500 ream and a dry tensile strength of 0.9 lbs. per inch. The paper appears to be optically homogeneous (i.e., it becomes invisible) when immersed in toluene at room temperature because the gel structure has not collapsed.

Another part of the web is dried in an oven at 250° F. The air in this oven is not humidified. The paper shrinks about 13% in each dimension. The tensile strength of the dry paper is 4.0 lbs. per inch, and it remains visible as a cloudy stratum when immersed in toluene at room temperature.

A third part of the web is dried for one minute on a rotating laboratory drum drier having a surface temperature of 240° F. The web is held in dimensional restraint against the drum by the pressure of a dense paper dryer felt about 3/16" thick. The felt passes over the drying drum and a tensioning roll, and the felt is maintained under high tension by adjustment of the tensioning roll. The porosity of the felt permits the water vapor evolved by the web to escape, and the dense structure of the felt prevents access of atmospheric air to the web which when heated to 200° F. would have a sufficiently low humidity to cause the gel structure of the web to collapse non-uniformly with formation of vacuoles. It is estimated that as a result the paper is maintained in an atmosphere of roughly 90%–100% relative humidity during at least a preponderant part of its drying.

The tension of the felt prevents the major part of the shrinkage that would otherwise take place. Measurement of the web before and after drying shows that the web shrinks during the drying 2.0% transversely to its direction of travel and 9.3% in machine direction (i.e., along its direction of travel). From other experience it is know that the felt prevented a considerably greater contraction.

The water content of the resulting paper is 0.5% by weight, its basis weight is 49.9 lbs. per 25" x 40"/500 lb. ream and its tensile strength is 9.6 lbs. per inch.

The paper is optically homogeneous when immersed in toluene.

Results are tabulated as follows:

Sheet No.	Drying of Web			Dried Paper	
	Temp., °F.	Supra-Normal Rel. Humidity	Dimensional Restraint	Optical Homogen.	Tensile Strength Lb./In.[4]
1	75	No [1]	No	Yes	0.9
2	250	No [2]	No	No	4.0
3	250	Yes [3]	Yes	Yes	9.3

[1] Relative humidity normal; about 50%.
[2] Relative humidity normal; less than 4.5%.
[3] Relative humdiity 90%–100%.
[4] In machine direction.

The principal effect of dimensional restraint during the drying is to increase the rate at which the gel structure of the wet web can be made to collapse uniformly and completely. This fact and the results tabulated above show therefore that the critical step in the process is the maintenance of supra-normal relative humidity during the final phase of the drying.

Example 2

The following shows that the wet web must contain more than about 40% by weight of water prior to the start of the final drying step.

Several wet-gel webs are produced by the method of Example 1 and are pressed between felts to a water content of 80% by weight. The webs are then hung at

normal atmospheric temperature and humidity until they have respectively partially dried to the water contents shown in the table below. The handsheets are then completely dried under a paper drier felt on a laboratory rotary drier having a surface temperature of 240° F. as shown in Example 1. The felt presses the paper against the drum of the drier so as to prevent about half of the shrinkage that normally takes place and substantially entirely prevents access of dry air to the web as it dries. The optical homogeneity of the paper sheets thus obtained is determined by dipping the paper in toluene as described in Example 1. Results are as follows:

Sheet No.	H_2O Content of Web at Start of Drying [1] Percent	Optical Homogen.	Tensile Strength, Lb./In.
1	68	Yes	9.3
2	63	Yes	9.3
3	60	Yes	9.3
4	51	Yes	9.3
5	35	No	
6	8	No	
7	2	No	

[1] Sheets are dried to a water content of less than 1% by weight.

The results show that optically homogeneous sheets are not obtained unless the water content of the webs is in excess of about 35%–40% by weight at the start of the final drying step.

Example 3

The following illustrates the production of paper according to the present invention by drying the wet web without dimensional restraint in an atmosphere having a supra-normal relative humidity.

A wet-gel polyacrylonitrile handsheet prepared by the method of Example 1 containing about 70% by weight of water is placed in a controlled humidity oven having a dry bulb temperature of 230° F. and the humidity of the oven is adjusted by admission of live steam so that the wet bulb temperature is 157° F. This is equivalent to a relative humidity of 21%–22%.

Calculations from relative humidity tables show that the air in the oven contained 0.2533 g. of water per gram of dry air and that the ambient atmosphere (70° F., 70% R.H.) contained 0.0111 g. of water per gram of dry air.

The air in the oven consequently contained about 25 times the amount of water as was contained by the ambient atmosphere.

The handsheet is maintained in the oven for 45 mins. and then removed. The handsheet is dry and has a tensile strength of about 15 lbs. per inch. Its basis weight is 75 lb. per 25" x 40"/500 ream. The sheet is clear when immersed in toluene as described in Example 1, showing that the fibers of which it is contained are optically homogeneous. In this respect the paper is similar to Sheet No. 3 of Example 1, which was produced in one minute by drying the web under dimensional restraint.

Example 4

The following illustrates the preparation of a resin-bonded laminate comprising a sheet of polyacrylonitrile paper according to the present invention.

A glass plate 10" x 14" x ¼" carrying a mold release coating (a composition predominantly stearamide known as "ReleasaGen Type H–15–1" sold by General Mills Co.) is placed over one corner of a rectangular sheet of uncoated non-fibrous regenerated cellulose 24" x 40". About 30 g. of the resin binder solution described below is puddled on the plate, a sheet 10" x 14" of optically homogeneous polyacrylonitrile paper (Sheet No. 3 of Example 1) is placed on the plate and is saturated with added resin solution. More resin solution is poured on the saturated paper. A sheet of cellulose paper, printed with the design of mahogany wood, is laid face down on the assembly and is similarly saturated with the resin solution. A sheet of fiber glass mat is placed over the cellulose sheet and is similarly saturated, and more resin is added so that the mat carries a liquid coating of resin. The unoccupied part of the cellulose film is then folded over the laminate and air bubbles are worked out of the laminate by a squilgee pressing against the cellulose film. Finally, a duplicate glass plate is placed over 150° F. for 90 minutes and is further heated at 250° F. for 60 minutes until thermosetting of the resin is complete.

The product laminate is separated from the glass plates and cooled. It resembles a sheet of mahogany veneer in stiff, strong, glossy, transparent plastic. The index of refraction of the resin is sufficiently close to the index of refraction of the polyacrylonitrile sheet so that the sheet appears to be transparent and invisible.

When the procedure is repeated using paper which is not optically uniform (Sheet No. 2 of Example 1), the product laminate resembles a sheet of mahogany veneer set is stiff, strong, glossy plastic which is largely as translucent as if it were a layer of frosted glass.

The resin binder solution is prepared as follows. A polyester resinous composition containing reactive ethylenically unsaturated polyester resin prepared by condensing phthalic anhydride, maleic anhydride and ethylene glycol in 1:1:2.1 molar ratio respectively in the presence of 0.1% by weight of t-butyl catechol and 0.1% by weight of triphenyl phosphate. To three parts by weight of this resin is added one part of monomeric styrene.

To 200 g. of the above resinous mixture is added with stirring first 39 g. of inhibitor-free methyl methacrylate and then 0.48 ml. of a 25% by weight solution of benzyl trimethyl ammonium chloride in water-diethylene glycol, 1.91 ml. of a solution of copper naphthenate solution in styrene, the solution containing 0.01% Cu by weight, 1.2 g. of benzoyl peroxide, and 1.68 ml. of cumene hydroperoxide. The solution is stirred until uniform and is then degassed under vacuum.

We claim:

1. In a continuous process for the manufacture of paper wherein an aqueous suspension of wet-spun wet-gel fibrillated polyacrylonitrile paper-making filaments of a polymer predominantly composed of acrylonitrile is continuously sheeted to form a water-laid web, and said web containing at least about 40% by weight of free and combined water and being composed of filaments having a gel structure is continuously dried at a temperature between about 150° F. and the decomposition point of the polymer of which said filaments are composed, the improvement which comprises substantially continuously maintaining said web in an atmosphere having at least 20% relative humidity during said drying until said gel structure has substantially completely collapsed.

2. A process according to claim 1 wherein said web is maintained in an atmosphere of 90%–100% relative humidity during at least a preponderant part of said drying.

3. A process according to claim 1 wherein the atmosphere of supra-normal relative humidity is provided by drying the web between an impermeable metal surface and a paper machine felt.

4. A process according to claim 1 wherein the atmosphere of supra-normal relative humidity is provided by drying the web between two paper machine felts.

5. A process according to claim 1 wherein the web is maintained under dimensional restraint during said drying and heat-bonding.

6. Paper prepared by a process according to claim 1.

7. Paper prepared by a process according to claim 1, uniformly impregnated with and coated by a transparent

resin; the index of refraction of said paper and of said resin being sufficiently alike to render said paper apparently transparent.

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DONALL H. SYLVESTER, *Primary Examiner.*

MORRIS O. WOLK, *Examiner.*

H. R. CAINE, *Assistant Examiner.*