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POROUS, ACID-RESISTING DIAPHRAGM.

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To all whom it may concern:

Be it known that I, LAMAR LYNDON, a citizen of the United States, residing in the city of New York, county and State of New York, have invented certain new and useful Improvements in Porous, Acid-Resisting Diaphragms, of which the following is a specification.

This invention relates to the production of porous materials for separators in electric batteries, diaphragms for filtration or for electrolytic processes, and uses of a like nature.

In a patent application of even date, Serial No. 452,585, I disclose a new, porous, acid-resisting material. This other application covers the general treatment of cellulose with an acid, whereby a chemical compound is formed which is soluble in certain solvents. After treating this compound with such a solvent, the material is rolled or pressed into sheets, the relation between the degree and character of the acid treatment and the character and dilution of the solvent being such that the resultant material is porous.

In the practice of my invention, I find that excellent results are obtained by the use of cellulose in some organized form, such as cotton cloth or cotton felt. While cotton in these forms is more expensive than raw cotton, the processes of manufacture are so facilitated by the use of organized materials and the final product is so much better than that made from raw material, that it is advantageous to use an organized material (fabric) for the substance which is nitrated.

I have found in practice that excellent results are obtained with an open mesh thin fabric, using several layers of such material to make my diaphragms, rather than a single layer of a thicker fabric, not only because of enhanced porosity, but, also, because of the greater ease, speed and uniformity of manufacture.

The first step in my process is to immerse the cotton or felt in a bath of mixed nitric and sulphuric acids. This may be done in different ways. I may pass the material, for instance, from a roll, or in some similar fashion, through the aforesaid bath of mixed nitric and sulphuric acids, at a rate that will give a continuous period of immersion corresponding to the particular degree of nitration of the case, the latter being more fully explained further below, or the fabric may be cut into small sheets and immersed in said bath. In either case, the bath will be stirred during the process. When using a thin material, I prefer to form it into layers, whether it be rolled, as above described, or cut into pieces, before immersing it in the bath. The weight of the acids in the bath which effects the nitration should be at least twenty five times the weight of the total material treated. The acids should be substantially concentrated, i. e., the specific weight of the nitric acid should be preferably from 1.51 to 1.54, and that of the sulphuric acid from 1.836 to 1.842, although I found that less concentrated acids will also produce the desired result, with some modification in the succeeding steps of my process, not affecting it in principle, but calling for somewhat different proportions as to degrees of solution, time, and the other factors entering into my process and more fully described further below. The standard proportion of nitric and sulphuric acids in the well known processes of nitration varies greatly, from one in which the proportion of nitric to sulphuric is 1 to 3, to one in which this proportion is reversed, i. e., wherein the proportion of nitric to sulphuric is 3 to 1. I have found satisfactory results within this wide variation of the commercial processes of nitration, although, of course, proportions in the succeeding steps of my process would naturally vary to correspond to the variation in the consistency of the bath, at least, to some extent, without, however, affecting the general procedure. In the examples given below, the bath contained equal proportions of nitric and sulphuric acids. According to the consistency of the bath, temperature, and thickness of the material immersed in the bath, the immersion may vary from two to fifteen minutes, although the best results have been obtained by me when the immersion lasted from four to seven minutes. The period of immersion will be greater when the thickness of the material is greater. The length of the period of immersion will also be increased with the lowering of the temperature, although, usually, normal room temperature would be used. Finally, the period of immersion will be the greater, the less the proportion of nitric acid in the bath. The best and the safest way of determining the necessary degree of nitration which is also a sufficient way for those skilled in the art, is to say that the weight

of the nitrated cellulose should be from forty to seventy per cent greater than the weight of the original cellulose. These limits are necessary limits, but, for practical purposes, the limits should remain between forty five and sixty five per cent, to obtain good results.

The next step in my process is to remove the nitrated cellulose from the bath, to wash it thoroughly, so that practically all of the residual acid is removed therefrom, and then either dry it, or de-hydrate it in some manner, such as, for instance, by the use of alcohol.

The next thing to do is to treat the dried or de-hydrated material with a suitable solvent. Any collodion-forming solvent may be used. I have found that good results are obtained by using a mixture of ethyl acetate and alcohol in the proportion of 10 c. c. of ethyl acetate to 28 or 30 c. c. of alcohol, when the increase in weight of the material due to nitration was from 50% to 60%.

The fourth step in my process is to arrest the dissolving operation before the nitrated cellulose becomes a collodion throughout and, later, a solid, impervious mass, my process requiring that the nitrated cellulose be only partially attacked by the solvent. The arresting moment is determined by the change which takes place on the surface of the material. The dissolving process is arrested as nearly as possible at the moment when the surface of the substance begins to become slimy, as it does in practice.

The fifth step in my process is to submit the thus partially dissolved, nitrated cellulose to heat and pressure. If the original fabric was not formed into several layers before being immersed in the bath of nitric and sulphuric acids, the forming of the material into layers may be made either after nitration, or after the nitrated cellulose is partially dissolved, as specified, and before it is submitted to heat and pressure. For the latter purpose, I may use pressure rollers heated before the material is passed between them, the temperature of the rollers being successively increased with each such passage, starting at a comparatively low temperature of from 120 to 140 degrees F., and raising it with each successive rolling operation until the temperature reaches from 210 to 225 degrees F. The amount of pressure may vary according to circumstances, but this is a matter subject to regulation and not requiring especial directions. The only prerequisite is that the pressure be sufficiently high to weld the layers together into an integral, solid sheet.

As an alternative to treating the dried or de-hydrated material with such a solvent as described in the third step of my process, I may use a solution of gum camphor in alcohol. In this case, the arresting feature of my process lies in the limitation imposed on the proportion of camphor in its solvent (alcohol or benzol, for instance), viz, the proportion of camphor should be from 10% to 35% by weight, corresponding to 90% and 65% weight of the solvent. Good results have been obtained by me with a solution in the proportion of from one to one and a half ounces of camphor to one pint of alcohol, when the increase in weight of the material after nitration was between 50% and 60%. After treatment with the camphor solution, the material is allowed to dry to some extent before passing it through the pressure rollers and submitting it to heat in the manner above described. It is preferable to have the material somewhat moist before pressing it into a sheet.

It is to be understood that the herein mentioned figures on the various proportions of the factors entering into my process are subject to wide variations and that, in general, various changes, omissions and substitutions in my process, as disclosed, may be made by those skilled in the art, without departing from the spirit of my invention. Nor do I limit myself to the specific ingredients described above in obtaining my porous diaphragms, and, when I use the word "pyroxylin" in the claims, which follow, I mean, quite generally, a chemical compound whereof the base is an acid-treated cellulose which is soluble in collodion-forming solvents.

I claim:

1. The process of making porous pyroxylin plastics, comprising the treatment of pyroxylin with a collodion-forming solvent until the surface of the resulting substance begins to become slimy, and then submitting said substance to heat and pressure.

2. The process of making porous pyroxylin plastics, comprising the treatment of pyroxylin with a collodion-forming solvent until the surface of the resulting substance begins to become slimy, and then compressing said substance into a sheet, the latter operation being accompanied by application of heat.

3. The process of making porous pyroxylin plastics, comprising the treatment of pyroxylin with a collodion-forming solvent until the surface of the resulting substance begins to become slimy, and then compressing said substance into a sheet through a succession of treatments at rising temperatures.

4. The process of making porous pyroxylin plastics, comprising the treatment of pyroxylin with a collodion-forming solvent until the surface of the resulting substance begins to become slimy, and then submitting said substance to successively increasing pressure accompanied by application of heat at rising temperature.

5. The process of making porous pyroxy-

lin plastics comprising the treatment of pyroxylin with a collodion-forming solvent until the surface of the resulting substance begins to become slimy, and then compressing said substance into a sheet by a series of operations involving the application of heat and pressure, said operations beginning with a temperature of from 120 degrees F. to 140 degrees F. and ultimately reaching a temperature of from 210 degrees F. to 225 degrees F. by successive increases.

6. The process of making porous pyroxylin plastics, comprising the treatment of pyroxylin with a collodion-forming solvent until the surface of the resulting substance begins to become slimy, and then passing said substance through pressure rollers under heat at rising temperatures.

7. The process of making porous pyroxylin plastics, comprising the treatment of pyroxylin with a collodion-forming solvent, said treatment being arrested before the material becomes wholly a collodion, and then submitting the material to pressure accompanied by heat.

8. The process of making porous pyroxylin plastics, comprising the treatment of pyroxylin with a collodion-forming solvent, said treatment being arrested before the material becomes wholly a collodion, and then compressing said material into a sheet in successive operations accompanied by heat at rising temperatures.

9. The process of making porous pyroxylin plastics, comprising treatment of a pyroxylin fabric with a collodion-forming solvent until the surface of the resulting substance begins to become slimy, and then submitting said substance to heat and pressure.

10. The process of making porous pyroxylin plastics, comprising treatment of a pyroxylin fabric, made up of a multiplicity of layers with a collodion-forming solvent until the surface of the resulting substance begins to become slimy, and then welding said layers together into an integral, solid mass by submitting them to pressure accompanied by the application of heat.

11. The process of making porous pyroxylin plastics, comprising treatment of a pyroxylin fabric with a collodion-forming solvent until the surface of the resulting substance begins to become slimy, the material being formed into a plurality of layers, and then welding said layers together into an integral, solid sheet, by submitting said layers to successive pressure operations, said operations being accompanied by heat at successively increased temperatures.

12. The process of making porous pyroxylin plastics, comprising treatment of a pyroxylin fabric, formed into a plurality of layers, with a collodion-forming solvent, said treatment being arrested before the material becomes wholly a collodion, and then submitting said material to a succession of pressure and heat operations, the pressure and the heat being increased with each successive operation.

13. The process of making porous pyroxylin plastics, comprising treatment of a pyroxylin fabric with a collodion-forming solvent until the surface of the resulting substance begins to become slimy, the material being formed into a plurality of layers, and then welding said layers into an integral, solid sheet, by submitting them to successively increasing pressure, the latter operation being accompanied by the application of heat at successively rising temperature beginning with a temperature of from 120 to 140 degrees F. and ultimately reaching a temperature of from 210 to 225 degrees F.

14. The process of making porous pyroxylin plastics, comprising the treatment of pyroxylin with a solvent, but permitting said solvent to combine with said pyroxylin only to a limited degree, and then submitting the resulting substance to heat and pressure.

15. The process of making porous pyroxylin plastics, comprising the treatment of pyroxylin with a solvent, the amount of said solvent being less than that which said pyroxylin is capable of combining with, and then submitting the resulting substance to heat and pressure.

New York, March 14th, 1921.

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