

UNITED STATES PATENT OFFICE.

CARL DANIEL EKMAN, OF LONDON, ENGLAND.

PROCESS OF OBTAINING ADHESIVE FROM SULFITE LIQUORS.

SPECIFICATION forming part of Letters Patent No. 550,712, dated December 3, 1895.

Application filed December 1, 1893. Serial No. 492,546. (No model.) Patented in England October 24, 1893, No. 20,036; in Germany December 1, 1893, No. 81,643; in France January 30, 1894, No. 235,927; in Sweden March 8, 1894, No. 5,923; in Hungary March 9, 1894, No. 123; in Italy March 13, 1894, No. 35,773/162; in Austria March 20, 1894, No. 44/569; in Canada July 5, 1894, No. 46,492, and in Norway October 26, 1894, No. 3,820.

To all whom it may concern:

Be it known that I, CARL DANIEL EKMAN, of London, England, have invented certain new and useful improvements in obtaining useful products from the liquors resulting from the manufacture of cellulose or fibers by the sulphite process, of which the following is a specification.

This invention is the subject-matter of Letters Patent in Great Britain, No. 20,036, dated October 24, 1893; in Germany, No. 81,643, dated December 1, 1893; in France, No. 235,927, dated January 30, 1894; in Sweden, No. 5,923, dated March 8, 1894; in Hungary, No. 123, dated March 9, 1894; in Italy, No. 35,773/162, dated March 13, 1894; in Austria, No. 44/569, dated March 20, 1894; in Canada, No. 46,492, dated July 5, 1894, and in Norway, No. 3,820, dated October 26, 1894.

The object of this invention is to obtain useful products from the liquors (hereinafter called the "sulphite liquor") resulting from the manufacture of cellulose or fibers from wood or other fibrous plants by boiling under pressure with a sulphite solution or a solution containing sulphurous acid and a base, such as potash, soda, magnesia, or lime.

My invention when carried out to its fullest extent is a process or method of treatment which consists in first making the sulphite liquor alkaline by means of a suitable base, then concentrating it, then adding to it a small quantity of a suitable acid or alum, sulphate of alumina, or bisulphate of soda to improve its color, then separating from the liquor a product resembling or having properties similar to those of dextrine, accomplishing this by decreasing the solubility of this product relatively to the liquor, as by adding to the latter a soluble salt in a solution of which in said liquor said product is partially insoluble or from which solution it separates, continuing such addition until said product separates from the liquor by rising to the surface and can be removed therefrom, and then after removal of the said dextrine-like product adding gelatine or glue to the liquor to obtain a product suitable for sizing and mordanting, and at the same time to separate or recover the salts that were used

for separating the dextrine-like product. It is, however, not an essential point of my invention that the process or method of treatment hereinbefore described should be carried out in its entirety, because useful products in a commercial and marketable form are obtained by carrying out only some of the stages or steps hereinbefore given, and the invention therefore includes processes or methods of treatment which comprise only some of said stages or steps. For example, it is not essential to render the sulphite liquor alkaline or to add an acid thereto before adding to it a soluble salt, as hereinbefore described, in order to obtain a dextrine-like product; but nevertheless I find that the obtaining of this dextrine-like product is much better effected and the product is of better quality when the sulphite liquor has previously had an acid added to it, as described, while the liquor need not be made alkaline if lead vessels are employed. Further, the addition of gelatine or glue to the liquor after the dextrine-like product has been separated and removed may be dispensed with if for any reason it may be preferred not to obtain the product suitable for sizing and mordanting or to recover the salts that were employed for separating the dextrine-like product.

Having stated what are the nature and main features of my invention, I will now describe how it can be carried into effect.

In carrying out the invention after the sulphite liquor has been clarified by settling or filtration I concentrate it by evaporation to a suitable thickness, which will vary according to the purpose for which it is to be used—say, for example, a specific gravity of about 63° Twaddle at a temperature of 85° centigrade. The evaporation should be effected in such manner that the liquor is not burned or overheated. A convenient way of obtaining the required heat is to employ a steam-coil or steam-jacket, the liquor being placed in a pan or vessel, which should be of a material which will resist the action of the liquor. When a steam-coil is used for heating the liquor, either the said coil should be made of lead or other material which will resist the action of the acid in the liquor; or if

it is desired to use evaporating-pans of iron or other materials which will be affected by the acids in the liquor the liquor should be made slightly alkaline by mixing with it a suitable base, such as potash, soda, and magnesia. These can be used in the state of caustics or carbonates; but if magnesia is employed well-burned magnesite in fine powder answers well when intimately mixed with the liquor while hot. Sufficient of the base should be added to cause the liquor to produce an alkaline reaction on red litmus-paper. After the liquor has been concentrated I preferably add a small quantity of a suitable acid to improve the color; or when a base is not added to the liquor, as before described, before evaporation the acid can with advantage also be added after concentration. Sulphuric or hydrochloric acid is suitable for the purpose, and the proportion used can be varied as desired, it being understood that the greater the amount of acid used up to a certain point the lighter will be the color of the liquor; but there should be no free sulphuric or hydrochloric acid in the liquor. Oxalic acid gives a good color, but it has the disadvantage of forming insoluble compounds with magnesia and lime. These can, however, be removed by settling and decantation if the liquor is not concentrated to a very thick state, or water can be added to it and the liquor be again evaporated to the desired degree of concentration; or I can use alum, sulphate of alumina, or bisulphate of soda instead of an acid in order to improve the color of the liquor.

The product obtained as above described is hygroscopic.

I employ this paste for the manufacture of further products and more particularly of a product resembling or having properties similar to those of dextrine and therefore readily soluble in cold water. In order to manufacture or obtain this dextrine-like product, I separate it from the organic substance which gives the liquor the hygroscopic property already mentioned. For this purpose I add to the liquor when hot (preferably after treatment, as hereinbefore described, although I can use the liquor in its original state, but by preference more or less concentrated) one or more of certain soluble salts, in a solution of which in such liquor the dextrine-like material contained in the liquor is partially insoluble or from which solution it separates, and I continue such additions until the dextrine-like material separates out. The solubility of the dextrine-like material is thus decreased relatively to the resulting liquor, and therefore it rises to the surface. This result is due to a physical process. No new chemical compound is formed, and as no new chemical compound is formed the salt that was added can be subsequently recovered. Suitable salts for this purpose are sulphates of potash, soda, or magnesia, alumina or ammonia, and chlorides of potash and soda. I have obtained the most satisfactory results

and best colors with the sulphates mentioned, and of these I prefer sulphate of magnesia. It is generally better, both as regards the quality of the products obtained and the carrying out of the process, to add alum or sulphate of alumina to one of the salts mentioned. I have also used sulphate of ammonia; but it has given less satisfactory results and is more difficult to manipulate. I keep on adding the salt or salts (they can be used alone or mixed) so long as the dextrine-like product continues to separate from the liquor. The dextrine-like product may be removed from time to time as it is formed, or when enough salt has been added the liquor may be allowed to remain in a hot state, when the dextrine-like product will go to the top and the liquor can be drawn off from the bottom of the vessel. The quantity of salt to be used varies according to the concentration of the liquors, the kind employed, and also according to the particular sulphite liquor to be treated, but taking as an example a sulphite liquor which has been obtained by boiling wood under pressure with a solution of bisulphite of magnesia or sulphurous acid and magnesia and which has subsequently been evaporated, as hereinbefore described, to a specific gravity of about 63° Twaddle at 85° centigrade, the liquor having first been made alkaline or not, as may be convenient, and an acid added, as above described. To three hundred parts, by weight, of the treated liquor I add about one hundred parts of sulphate of magnesia, and I continue the heating, stirring the liquor until all the salt is dissolved. The dextrine-like product rises to the top and forms a soft crust, which may be removed, and the process may be continued as long as more dextrine-like product is separated, or if left hot the liquor can be drawn off from the bottom, as before described. The dextrine-like product should be removed with care, so that as little liquor as possible may adhere to it. The dextrine-like product when cold forms a stiff mass, which may be dissolved so as to be used in a liquid form, or it may be dried preferably at a low temperature and be reduced to a powder, so as to be used like powdered dextrine.

If a more purified product is desired, the dextrine-like product obtained as above is dissolved in water and again separated by means of a salt, as above described, and this operation can be repeated as often as may be thought necessary.

The dextrine-like product obtained as above described, if mixed with a solution of gelatine or glue, forms a very concentrated material, which when dissolved by means of a suitable solvent, as a solution of sulphite of soda in water, can be used for mordanting or sizing textile fabrics or sizing paper.

The sulphite liquor contains another organic substance besides the dextrine-like material. This other substance has a very great affinity for water and does not part with it.

Therefore this organic substance remains in solution.

To the solution left after the separation of the dextrine-like product from the sulphite liquor, as above explained, I add a solution of gelatine or glue and allow it to separate, more and more gelatine or glue being added until no more product is formed. The product is of better color and separates more easily if alum or sulphate of alumina has been added either before separating the dextrine-like product or afterward. The product thus obtained becomes a dense mass on cooling; but it is desirable to remove as much as possible of the liquor adhering to it, and this can be effected by pressing or kneading or by washing when in a disintegrated state in a liquid which will not dissolve the product, such as a weak solution of a suitable salt, as a bisulphite or alum solution, or in a limited amount of water if alum has been added before. The product thus obtained, after having been properly dissolved, is suitable for sizing and mordanting.

The still remaining liquor is left to cool, when the salt which has been employed will partly crystallize. The liquor is then drawn off and can be further evaporated and again left to crystallize, and this operation can be repeated as long as any salt can be obtained by crystallization.

What I claim, and desire to secure by Letters Patent, is—

1. The method of treating the liquor resulting from the manufacture of cellulose or fibers by the sulphite process, and containing in solution a dextrine-like material, which method consists in separating such material from the

liquor as a dextrine-like product which is readily soluble in cold water, and rises to the surface of the liquor, by adding to the liquor a soluble salt in a strong solution of which salt in such liquor such dextrine-like material is partially insoluble, until such material separates from the liquor, substantially as hereinbefore described.

2. The method of treating the liquor resulting from the manufacture of cellulose or fibers by the sulphite process, and containing in solution a dextrine-like material, which method consists in separating out such material as a dextrine-like product, which is readily soluble in cold water, and rises to the surface of the liquor, by adding to the liquor sulphate of magnesia, substantially as hereinbefore described.

3. The method of treating the liquor resulting from the manufacture of cellulose or fibers by the sulphite process, and containing in solution a dextrine-like material, which method consists in separating said material from the liquor as a dextrine-like product which is readily soluble in cold water, and rises to the surface of the liquor, by adding to the liquor sulphate of alumina and another soluble salt in an amount which is in excess of what is soluble in cold water, until said material becomes so far insoluble that it separates from the liquor, substantially as hereinbefore described.

In witness whereof I have hereunto signed my name in the presence of two subscribing witnesses.

CARL DANIEL EKMAN.

Witnesses:

JOHN C. MEWBURN,
GEORGE C. BACON.