

UNITED STATES PATENT OFFICE

1,964,646

TREATMENT OF CELLULOSIC MATERIALS

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No Drawing. Application June 2, 1931, Serial No. 541,662. In Great Britain August 16, 1930

10 Claims. (Cl. 127—37)

This invention relates to the conversion of cellulose or cellulosic materials into dextrins, sugars and other conversion products and more particularly to the recovery of the acids employed for the conversion.

It has long been known that cellulose and cellulosic materials can be transformed or converted into dextrins, sugars or other conversion products by first dissolving them in strong acids (particularly sulphuric acid of 65 to 80% strength). In such process the solution is precipitated by the addition of water to isolate the primary conversion products (e. g. acid celluloses and the like), or, in the case where it is desired to obtain products of further conversion (e. g. dextrins, sugars and the like) the solution is diluted until a low acidity (e. g. about 1% to 5%) is attained and subjected to a higher or boiling temperature. Whilst this method of treatment of cellulose or cellulosic materials enables highly satisfactory yields of the conversion products to be attained, it suffers from the great disadvantage that the acids are used very wastefully. Thus in the case where the conversion products are to be isolated from the "cellulosic solution" (i. e. the solution formed by the action of the strong acid) a very extensive dilution is necessary to obtain the desired precipitation, thereby necessitating expensive concentration of the dilute aqueous acids if they are to be employed as a source of concentrated acids for the treatment of cellulose or "cellulosic solutions." Further, in the case where it is desired to obtain products of further conversion from the "cellulosic solutions", the use of the acid is highly wasteful, as it is necessary to neutralize the acid (e. g. with $\text{Ca}(\text{OH})_2$, CaCO_3 , etc.) in the solutions resulting from the dilution and further conversion treatment in order to separate the dextrin, glucose, sugars or the like from the solutions.

In accordance with the invention we transform cellulose or cellulosic materials into conversion products by a process comprising treating the cellulose or cellulosic materials with strong acids, preferably until complete solution of the cellulose or cellulosic materials is effected, and thereafter extracting the acid with acetone. By this means the acid can be separated in a very satisfactory manner from the primary conversion products, the acid dissolving in the acetone whilst the conversion product remains behind as a granular or like insoluble mass. The acid may be extracted entirely or substantially so or to any desired degree by the acetone.

Owing to the high volatility of acetone the acid can readily be concentrated to its original strength and made to serve for the treatment of further quantities of cellulose or cellulosic materials. Further, the acetone can be used for extraction of acid from further "cellulosic solutions".

In cases where it is desired to transform the primary conversion product into products of transformation (e. g. dextrins, sugars and the like) the primary conversion product may be subjected to the necessary action of dilute acid in any convenient way. For instance the primary conversion product after extraction of all or substantially all acid in the manner above indicated may be placed in dilute acid (e. g. sulphuric acid at about $\frac{1}{2}$ to 5% strength) and subjected to a hot or boiling temperature with or without pressure. Preferably, however, we perform the acetone extraction in such manner as to leave a small quantity of acid in the primary conversion product such as is sufficient to enable the further conversion to take place on heating or boiling the product in water.

The process of the invention may be applied to the treatment of cellulose or cellulosic materials, as for instance wood, straw, grasses, cotton, wood pulps (e. g. sulphite, sulphate or soda pulps), reconstituted cellulose. Preferably the cellulose or cellulosic materials are employed in a fine form, e. g. cotton fibres, cotton linters, wood pulps, in the form of fine chips, sawdust, ground mechanical wood pulp.

In performing the invention cellulose or the cellulosic materials may be treated with the strong acids in any convenient manner. Thus for instance the materials may be treated with strong sulphuric acid of about 65 to 80% strength, and particularly of 70 to 80% strength. The treatment may be performed at low or ordinary temperatures, or at somewhat higher temperatures (e. g. between about 25 to 35° C.). Temperatures of between about 28 to 33° C. are found to be especially useful. We prefer to use fairly restricted quantities of the strong acid relatively to the cellulose or cellulosic materials, for example an amount of actual acid (i. e. H_2SO_4 as distinct from the actual liquor) not exceeding twice the weight of the cellulose present, and preferably in an amount between about $\frac{3}{4}$ and $1\frac{1}{4}$ of the weight of the cellulose present.

The cellulose or cellulosic materials and the strong acids can, of course, be mixed together in any convenient way. For instance the cotton or other cellulose or cellulosic materials can be

added in stages to the strong acid, if desired the addition of further quantities of cellulosic materials being deferred until that already added has gone into solution. The mixture of strong acid and cellulosic materials, irrespective of the mode of addition of the materials together, is preferably subjected to kneading or stirring to ensure uniform action of the strong acid.

The time necessary for the strong acid to effect the necessary action upon the cellulosic materials may vary with the temperature and strength of the acid and the degree of division of the cellulose or cellulosic materials, the higher the temperature and concentration the less being the time necessary. Usually a time between about $\frac{1}{2}$ hour and 24 hours is sufficient. With sulphuric acid of about 70% strength and with a temperature of about 30° C. very useful results are obtained in between 6 and 10 hours.

The action of the strong acid upon the cellulose or cellulosic materials, particularly when the higher temperatures are employed, should preferably be kept as short as possible in order to avoid any substantial conversion of the primary conversion products into acetone soluble products of further conversion such as dextrans or sugars.

After the treatment with the strong acid the acid may be extracted by acetone in any convenient way as for instance by pouring the product into acetone. Upon treatment of the product with acetone the acid dissolves in the acetone and leaves the primary conversion product, usually in a granular form. The acid can be separated from the acetone solution for instance by heating to drive off the acetone by which means the acid can be readily recovered in a form sufficiently concentrated to enable its employment for treating further quantities of the cellulose or cellulosic materials. The acetone can of course be recovered and employed for separating the acid from a further quantity of "cellulosic solution".

The quantity of acetone necessary to remove the acid will of course depend upon the degree to which it is desired to remove the acid and the conditions of operation. Generally a quantity in amount about 3 to 5 times that of the acid present is sufficient to remove substantially all acid present. Advantageously the separated primary conversion product can be washed with acetone, such treatment being especially advantageous when it is desired to obtain the primary conversion product substantially free from acid.

In cases where it is desired to transform the primary conversion product into products of further transformation, such as dextrans or sugars, the further conversion can be effected in any convenient way. As before mentioned such further conversion can be effected by heating or boiling the primary conversion product under ordinary or raised pressure with a dilute acid (e. g. sulphuric acid of about $\frac{1}{2}$ to 5% concentration). Such treatment can, if desired, be effected by subjecting to the action of hot or boiling dilute acid a primary conversion product from which substantially all acid has been removed by the acetone. Preferably, however, a small amount of acid, e. g. about 5 to 20% of the acid originally employed for treating the cellulose or cellulosic materials is left in the primary conversion product, which product is then heated or boiled with water (under ordinary or raised pressure and preferably under reflux) until the desired stage of further conversion is attained.

The following example serves to illustrate a

convenient form of execution of the invention, but it is to be understood that the invention is in no way limited thereto.

Example

Cellulose or cellulosic material, e. g. wood pulp, cotton or the like is added in stages and with continual stirring to 78 to 79% sulphuric acid, the total quantity of sulphuric acid used being about twice the weight of the actual cellulose treated. During the addition of the cellulose or cellulosic material, and for a period of about four hours afterwards, the temperature is maintained at about 30° C., after which the solution obtained is stirred into acetone, the quantity of acetone being about twice the weight of the (78 to 79%) sulphuric acid originally employed.

The granular precipitate obtained upon addition of the "cellulose solution" to the acetone is washed with a further quantity of acetone, being about $\frac{1}{2}$ of the weight of the acetone employed for the first extraction, whereafter it may, if desired, be subjected to further conversion by hydrolysis.

The acetone solution of sulphuric acid is distilled to separate the acetone and sulphuric acid in order that they may be employed again.

What we claim and desire to secure by Letters Patent is:—

1. Process for the transformation of cellulosic materials into conversion products which comprises treating the cellulosic materials with sulphuric acid, and thereafter extracting the acid with acetone.

2. Process for the transformation of cellulosic materials into conversion products which comprises treating the cellulosic materials with a sulphuric acid of concentration between 50 and 80% and thereafter extracting the acid with acetone.

3. Process for the transformation of cellulosic materials into conversion products, which comprises treating the cellulosic materials with sulphuric acid at temperatures between 25° and 35° C., and thereafter extracting the acid with acetone.

4. Process for the transformation of cellulosic materials into conversion products which comprises treating the cellulosic materials with sulphuric acid in an amount of actual sulphuric acid at most twice the weight of the actual cellulose present, and thereafter extracting the acid with acetone.

5. Process for the transformation of cellulosic materials into conversion products which comprises treating the cellulosic materials with sulphuric acid, and thereafter extracting the acid with acetone in amount between 3 and 5 times the weight of the sulphuric acid to be extracted.

6. Process for the transformation of cellulosic materials into conversion products which comprises treating the cellulosic materials with a sulphuric acid of concentration between 70 and 80% in an amount of actual sulphuric acid of at most twice the weight of the actual cellulose present at temperatures between 25° and 35° C., and thereafter at least partially extracting the acid with acetone in amount between 3 and 5 times the weight of the sulphuric acid to be extracted.

7. In a process for the transformation of cellulosic materials into sugars, dextrans and like simple conversion products, treating the cellulosic materials with sulphuric acid, at least partially extracting the acid with acetone, and subjecting the product to hydrolysis.

5 10 15	8. In a process for the transformation of cellulosic materials into sugars, dextrans and like simple conversion products, treating the cellulosic materials with sulphuric acid, at least partially extracting the acid with acetone, and subjecting the product to hydrolysis by boiling with sulphuric acid of concentration between 0.5 and 5%. 9. In a process according to claim 7 the step of hydrolyzing the said product by means of part of the acid employed in the initial treatment and remaining after the acetone extraction, which acid is diluted by addition of water to a concentration of between 0.5 and 5%. 10. In a process for the transformation of cellulosic materials into sugars, dextrans and like	simple conversion products, the steps of treating the cellulosic materials with sulphuric acid of concentration between 70 and 80% in an amount of actual sulphuric acid of at most twice the weight of the actual cellulose present at temperatures between 25° and 35° C., partially extracting the acid with acetone in amount between 3 and 5 times the weight of the sulphuric acid to be extracted, diluting the acid remaining in the product with water to a concentration between 0.5 and 5% and boiling the said product in the said diluted acid. HORACE FINNINGLEY OXLEY. WALTER HENRY GROOMBRIDGE. WILLIAM CHALLIS.	80 85 90
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