Patented Mar. 16, 1943 2,313,866

UNITED STATES PATENT OFFICE

2,313,866

MANUFACTURE OF CELLULOSE ETHERS

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No Drawing. Application September 6, 1940, Serial No. 355,600

4 Claims. (Cl. 260—231)

This invention relates to an improved method for the alkylation of cellulose, and more particularly to an improved method for the alkylation of sheet cellulosic material to produce cellulose ethers of high quality and commercial acceptability.

Heretofore the art has manufactured cellulose ethers from cellulosic material by two general processes: The first process includes two steps, (1) the production of alkali cellulose by steeping cellulosic sheets in concentrated caustic alkali followed by the removal of the caustic liquid. This alkali cellulose is usually in the form of sheets known as pulp board and before being etherified must be disintegrated by a shredding machine and (2) the treatment of this alkali cellulose with an alkyl chloride such as, for example, ethyl chloride, and additional quantity of alkali, and, usually, a diluent such as benzene or toluene. This admixture is heated with vigorous stirring until etherification has proceeded to the proper degree. The first step comprising the production of alkali cellulose is a very expensive procedure as it requires considerable time, expensive ingredients and expensive equipment and it has been found by the art that although alkali cellulose will give high quality ethyl cellulose it is impractical to use it in commercial production due to the time and money required.

The second general method which has been developed to obviate the need of manufacturing alkali cellulose as an intermediate comprises a one step process in which the cellulose, alkali, water, etherifying agent and diluent are all added directly to a reaction vessel and heated with vigorous agitation until the proper degree of etherification is reached. This method simplifies the procedure by avoiding the separate production of alkali cellulose but gives a product that is non-uniform, and not of commercial quality. This method has not found commercial application in spite of its inherent simplicity.

Now I have found that I can entirely eliminate the mastication step or materially reduce the extended time which it has heretofore consumed and still obtain the uniform alkylation required for a satisfactory commercial product. I accomplish this by shipping a fibrous cellulosic material in form of a loosely felted sheet by the method described in U. S. Patent 2,028,080 to Raphael L. Stern, prior to the incorporation or wetting thereof with an aqueous alkali solution. By so doing, I not only effect a material saving in time and in power required for the mastication, but I also largely avoid the metal contamination heretofore introduced by the mastication step and I produced cellulose ethers of very high quality.

The advantages which I obtain by using this chipped cellulosic material rather than other forms of raw cellulose, in the preparation of the alkali cellulose, is due to the uniformity of the size of the particles and their tendency to partially retain the original sheet structure, conducive to the quick wetting and free swelling of the fibers during the formation of alkali cellulose. After shredding the sheet cellulosic material to a suitable size prior to the addition of aqueous alkali solution no masticating operation is required. All that is required to form an alkali cellulose is the uniform mixing of the chipped cellulosic material with the desired amount of the aqueous alkali solution either by a short stirring operation or by spraying the aqueous alkali upon the chipped cellulose.

By the method in accordance with this invention, a relatively thin sheet of loosely felted, fibrous cellulosic material is cut or chipped into lengths, preferably of a width less than the thickness of the sheet, and at the same time the lengths will be separated lengthwise into two or more lengths which, respectively, will be of a thickness less than the thickness of the sheet. Hereinafter, I shall refer to a cellulosic material which is cut or chipped in this way as "chipped cellulose." The resultant chipped cellulose is then uniformly admixed and incorporated with an aqueous alkali solution either by stirring or spraying and the admixture treated with an alkylating agent such as, for example, an alkyl halide, a dialkyl sulfate, etc., for a period of time sufficient to give a uniform alkylation of the cellulose. The resultant alkyl cellulose is then recovered from the reaction mixture by one of the methods known to the art.

The chipped cellulose formed by the cutting or chipping operation will be comprised of lengths of loosely felted fibers. The ends and surfaces of the lengths will be irregular and will have protruding fibers. The cellulose may conveniently be put into this form by cutting or chipping in the mechanism described in detail in U. S. Patent 2,028,080.

The cellulose which I utilize in the method in accordance with this invention will desirably be in the form of loosely felted, fibrous sheets and will be of any type suitable for chemical treatment. It may be, for example, wood pulp or cotton linters, of types suitable for chemical treatment, in the form of felted sheets. Thus, for example, the wood pulp I utilize may have an alpha-cellulose content of 88%, 95% or such

other percentage as may be suitable or desired for alkylation. The wood pulp may be bleached to a high white, or to any less degree which may be satisfactory for the purpose for which the ultimate cellulose ether is intended.

The sheet from which the thread-like or ribbon-like lengths of chipped cellulose will be formed may be, for example, of any commercial form of felted wood pulp or felted cotton linters, suitable for use in the manufacture of alkyl ethers of cellulose. The sheet may be of any width, depending upon the capacity of apparatus designed to cut off the thread-like lengths which I treat with an aqueous alkali solution. The sheet may be of a thickness within quite wide limits, say, from about 0.02 to about 0.05 inch.

By way of illustration and not by way of limitation, a sheet of lightly felted cellulose having a thickness of 0.030 inch may be used. The chipped lengths formed from this sheet will desirably have a length, of say, about ⅛ inch to about 2 inches and desirably about ¾ inch. They will desirably have a width of about 0.015 inch and a thickness of about 0.010 inch. These lengths having a thickness of about 0.010 inch, will be formed by the cutting of 0.015 inch widths of a length of ¾ inch from the sheet and separating lengthwise into three pieces. The lengths will be thread-like or ribbon-like depending upon their width. The separating of the lengths causes their upper and lower surfaces to be irregular or rough with protruding fibers. Their edges will be irregular or rough due to the tearing, as well as the shearing action, of the cutting edges of the chipping machine.

The amount of alkali used, preferably caustic soda, will be any quantity customarily used by the art in the alkylation of cellulose. I have found that it is usually desirable to use an amount of alkali within the range of about 10 mols to about 34 mols, and preferably within the range of about 16 mols to about 28 mols, to each mol of cellulose (calculated as $C_6H_{10}O_5$) present, depending upon the desired alkoxy content of the product. The concentration of the aqueous alkali solution which I utilize will desirably be adjusted for convenient incorporation or spraying of the above indicated quantities of the alkali with the chipped cellulose material, preferably the aqueous alkali will be 50% caustic.

The alkylating agent used may be an alkyl halide or any alkyl sulfate and preferably, an alkyl chloride. Thus, for example, an alkylating agent may be methyl chloride, dimethyl sulfate, ethyl chloride, ethyl bromide, diethyl sulfate, propyl chloride, propyl bromide, butyl bromide, butyl chloride, etc. An alkylating agent will, of course, be chosen which contains the alkyl group that is desired in the cellulose ether, and it will be found that the method in accordance with this invention is applicable to the production of any of the alkyl cellulose ethers heretofore known and highly advantageous therein. Cellulose ethers which may be prepared in accordance with my invention are methyl cellulose, ethyl cellulose, propyl cellulose, butyl cellulose, etc.

The amount of alkylating agent used may vary within wide limits. In preparing cellulose ethers having a good solubility in organic solvents, I prefer to use a large excess of alkylating agent. Thus, I may use 7–15 mols of alkyl chloride to each cellulose unit. The alkylating agent serves not only as a reactant, but also as a medium for the reaction, and a large part of the excess may be recovered unchanged at the end of the reaction.

This excess of alkylating agent may be replaced to a greater or lesser extent by an organic solvent, such as, for example, a lower aliphatic alcohol or ether, benzene, toluene, dioxan, etc. Which acts both as a diluent (medium for the reaction) and as a solvent for the cellulose ether formed. The alcohol used may be a lower aliphatic alcohol such as, for example, methanol, ethanol, n-propanol, isopropanol, n-butanol, etc. To avoid the formation of an excessive number of by-products, I prefer to use an alcohol containing the same alkyl group as that contained in the alkylating agent. The time required to complete the reaction in the presence of such diluent is greater, than when an excess of the alkylating agent serves as a medium for the reaction.

When using an alkyl chloride as an alkylating agent, as I prefer to do, the reaction is carried out in an autoclave, provided with a stirrer or constructed for rotating or tumbling motion to affect agitation. I thoroughly admix or wet the chipped cellulose with the aqueous alkali solution, introduce this caustic-cellulose admixture into the autoclave and then add ethyl chloride and, if desired, a diluent thereto. After all the ingredients of the alkylation mixture are in the autoclave it is heated either rapidly or gradually to reaction temperature. I find that it is advantageous to heat the mixture very gradually. A desired reaction temperature is determined largely by the reactivity and the amount of the alkylating agent present. Thus, when using ethyl chloride as an alkylating agent, a temperature within the range of about 90° C. to about 150° C. and preferably, within the range of about 100° C. to about 130° C. will be found satisfactory. It will be found that the higher the temperature, the more rapid the reaction, while the lower temperature results in greater uniformity.

As further illustration of the method in accordance with this invention I may cite the following examples:

Example I

Lightly felted sheet wood pulp having a thickness of 0.030 inch was chipped into lengths of about ¾ inch, a width of about 0.015 inch and a thickness of about 0.010 inch. One part by weight of this chipped or shredded wood pulp was covered with 14 parts by weight of a caustic soda solution having a concentration of 50% by weight and stirred for 15 minutes during which time the chips became thoroughly wetted. The resulting wetted cellulose and free caustic solution were transferred to a high pressure autoclave. About 4.5 parts by weight of ethyl chloride were then added to the autoclave and the reaction allowed to continue for a period of 12 hours at a temperature within the range of about 80 to 140° C. The ethyl cellulose was then precipitated from the reaction mixture by distilling out the residual ethyl chloride and by-product ethyl ether and ethyl alcohol formed by the reaction, and then washed with water to remove the excess alkali and the sodium chloride formed by the reaction. The resulting ethyl cellulose was found to be as good as that produced from unshredded wood pulp sheets which had been first converted to alkali cellulose by being masticated for a period of 4 hours after

soaking for a period of 8 hours in a caustic soda solution.

EXAMPLE II

One part by weight of shredded sheet cotton linters was mixed with 14 parts by weight of a 50% aqueous solution of caustic soda for 15 minutes. The resulting mass was transferred to an autoclave and ethylated by the procedure described in Example I. The finished product, having an ethoxy content of about 47.9% was found to give solutions of high clarity and to be a commercially acceptable product. It was found to be definitely superior with respect to solution clarity and content of unethylated fibers to a product resulting from a comparable ethylation of alkali cellulose produced by the addition of one part, by weight of unshredded sheet cotton linters to 14 parts, by weight, of 50% aqueous caustic in a standard masticator within a period of 30 to 45 minutes, followed by mastication for two (2) hours with cooling.

EXAMPLE III

One part by weight of lightly felted cotton linter sheets were chipped in accordance with Example I and the chipped material sprayed with about 13 parts by weight of 50% sodium hydroxide solution. The chips wetted by the aqueous caustic were charged directly into an autoclave and about 4.3 parts by weight of ethyl chloride added thereto. The mass was continuously stirred for about 12 hours during which period the temperature was raised to about 140° C. The volatile organic solvents were then distilled from the autoclave and the ethyl cellulose recovered from the spent caustic. The product produced was of high quality and gave clear solutions.

In accordance with the procedure of Example III series of ethylations were carried out using first sheeted cotton linters and second clipped cotton linters, as the cellulose material. The ethyl cellulose produced in each ethylation was tested for turbidity with a Betz-Hellige Turbidimeter and showed the results given below in Table I.

Table I

Cellulose sample A	Turbidity of samples	
Run	Sheet cellulose	Chipped cellulose
1	1.7	1.4
2	1.7	1.0
3	1.8	1.1
4	1.6	0.9
Average turbidity	1.7	1.1

Cellulose sample B	Turbidity of samples	
Run	Sheet Cellulose	Chipped Cellulose
1	1.3	0.8
2	1.2	0.7
3	1.4	0.8
4	1.2	0.5
5	1.6	0.7
Average turbidity	1.34	0.7

From the above results it is obvious that the turbidity of ethyl cellulose solutions is greatly improved by the use of the chipped cellulose in accordance with this invention. The Betz-Hellige Turbidimeter is a standard instrument and the results are expressed as grams of barium sulphate per 60 cc. of distilled water measured at a depth of 20 mm. In the runs above the only variable introduced in the manufacture method, Example III, was the form of the cellulose used. The mechanical advantage of eliminating the expensive and time consuming mastication operation and the improved quality of cellulose ether produced especially as to turbidity which are accomplished by the method of my invention are definite advantages in the ethyl cellulose art and are possible only through the use of chipped cellulose.

The difference in the chipped cellulose and sheet cellulose is specifically shown by a comparison of the bulk density of the two materials. Bulk density is determined as pounds of material under its own weight, per cubic foot. Some bulk density values of sheeted cotton linters and wood pulp and chipped cotton linters and wood pulp are given in Table II below and conclusively demonstrate the extreme bulkiness of the chipped cellulosic material.

Table II

Sample	Bulk density	
	Shredded	Sheeted
	Lbs./cu. ft.	*Lbs./cu. ft.*
Cotton linters	3.8–4.2	21–35
Wood pulp	2.4–3.1	20–50

The process in accordance with my invention allows the production of cellulose ethers from cellulosic material in a simplified manner and provides a high quality product which shows improvement over prior art products in clarity of solutions and a decrease in the amount of unetherified particles. The invention provides a cellulosic material which is obtainable at a reasonable price, is easy to handle, requires no mastication process, is easily wetted, and produces a product of good color and solubility.

It will be understood that the details and examples hereinbefore set forth are illustrative only and that the invention as broadly described and claimed is in no way limited thereby.

This application is a continuation-in-part of my copending application, Serial No. 226,687, filed August 25, 1938.

What I claim and desire to protect by Letters Patent is:

1. A process for manufacturing cellulose alkyl ethers low in turbidity and soluble in organic solvents from lightly felted sheet cellulose composed of fibers selected from the group consisting of wood and cotton cellulose fibers which consists in chipping the sheet cellulose to thread-like or ribbon-like lengths and separating the lengths longitudinally to form chipped lengths having rough irregular ends and surfaces with protruding fibers, an open physical structure conducive to quick uniform wetting by aqueous alkali solution, and an apparent bulk density between about 2.4 and about 4.2 pounds per cubic foot; uniformly wetting the said chipped lengths with an aqueous solution of alkali metal hydroxide of a concentration forming alkali cellulose capable of reacting with an alkylating agent to form a cellulose ether soluble in organic solvents by lightly agitating the chipped lengths for not more than 15 minutes with the alkali solution; heating the resulting wetted cellulose

with a lower alkyl etherifying agent under etherifying conditions until a cellulose ether soluble in organic solvents is obtained; and recovering the cellulose ether.

2. A process for manufacturing ethyl cellulose low in turbidity and soluble in organic solvents from lightly felted sheet cellulose composed of fibers selected from the group consisting of wood and cotton cellulose fibers which consists in chipping the sheet cellulose to thread-like or ribbon-like lengths and separating the lengths longitudinally to form chipped lengths having rough irregular ends and surfaces with protruding fibers, an open physical structure conducive to quick uniform wetting by aqueous alkali solution, and an apparent bulk density between about 2.4 and about 4.2 pounds per cubic foot; uniformly wetting the said chipped lengths with an aqueous solution of alkali metal hydroxide of a concentration forming alkali cellulose capable of reacting with an ethylating agent to form ethyl cellulose soluble in organic solvents by lightly agitating the chipped lengths for not more than 15 minutes with the alkali solution; heating and agitating the resulting wetted cellulose with ethyl chloride under etherifying conditions at a temperature between about 90° C. and about 150° C. until ethyl cellulose soluble in organic solvents is obtained; and recovering the ethyl cellulose.

3. A process for manufacturing ethyl cellulose low in turbidity and soluble in organic solvents from lightly felted sheet cellulose composed of fibers selected from the group consisting of wood and cotton cellulose fibers which consists in chipping the sheet cellulose to thread-like or ribbon-like lengths and separating the lengths longitudinally to form chipped lengths having rough irregular ends and surfaces with protruding fibers, an open physical structure conducive to quick uniform wetting by aqueous alkali solution, and an apparent bulk density between about 2.4 and about 4.2 pounds per cubic foot; uniformly wetting the said chipped lengths with an aqueous solution of sodium hydroxide of a concentration forming alkali cellulose capable of reacting with an ethylating agent to form ethyl cellulose soluble in organic solvents in a quantity containing between about 10 mols and about 34 mols of sodium hydroxide for each $C_6H_{10}O_5$ mol of cellulose by lightly agitating the chipped lengths for not more than 15 minutes with the sodium hydroxide solution; heating and agitating the resulting wetted cellulose with ethyl chloride under etherifying conditions at a temperature between about 90° C. and about 150° C. until ethyl cellulose soluble in organic solvents is obtained; and recovering the ethyl cellulose.

4. A process for manufacturing cellulose alkyl ethers low in turbidity and soluble in organic solvents from lightly felted sheet cellulose composed of fibers selected from the group consisting of wood and cotton cellulose fibers which consists in chipping the sheet cellulose to thread-like or ribbon-like lengths and separating the lengths longitudinally to form chipped lengths having rough irregular ends and surfaces with protruding fibers, an open physical structure conducive to quick uniform wetting by aqueous alkali solution, and an apparent bulk density between about 2.4 and about 4.2 pounds per cubic foot; spraying the said chipped lengths with an aqueous solution of sodium hydroxide of a concentration of about 50% in a quantity containing about 10 and about 34 mols for each $C_6H_{10}O_5$ mol of cellulose and lightly agitating the sprayed chipped lengths for not more than 15 minutes, uniformly wetting out the cellulose thereby; heating and agitating the resulting wetted cellulose with ethyl chloride in a quantity of 7–15 mols for each $C_6H_{10}O_5$ mol of cellulose under etherifying conditions at a temperature between about 90° C. and about 150° C. until ethyl cellulose soluble in organic solvents is obtained; and recovering the ethyl cellulose.

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