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HYDROXYALKYLATION OF CELLULOSE AND DERIVATIVES

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4 Claims. (Cl. 260—231)

This invention relates to a process for the vapor-phase catalytic hydroxyalkylation of cellulose and cellulose derivatives; and, more particularly, it concerns such a process involving the use of a vapor-phase catalyst, in conjunction with the use of an alkylene oxide or mixture of such oxides in amounts ranging from 1% to 30% of the cellulose being hydroxyalkylated, and the employment of mild hydroxyalkylation conditions. The invention has especial utility for the production of cellulose derivatives eminently adapted for partial or complete esterification, and of derivatives readily peptizable in dilute caustic soda solutions for the preparation of films, filaments and other shaped objects, as well as for the hydroxyalkylation of paper stock prior to the formation of the web and calendered sheet to increase its absorbency. It also is applicable to the hydroxyalkylation of flax, hemp, ramie, and cotton yarns to alter their chemical properties, such as susceptibility to dyeing agents, wetting-out agents, etc., without altering the physical form of the yarn other than to increase its softness.

In the practice of the invention, air-dry cellulose,—i. e., cellulose containing from 2% to 10% of moisture,—is reacted with the vapor of an alkylene oxide, such as ethylene oxide and propylene oxide, in the presence of a tertiary amine that is also in the vapor-phase,—the reactions being conducted preferably at atmospheric pressure or subatmospheric pressure.

The reaction is so conducted that not substantially more than 30% of the alkylene oxide is combined with the cellulose. Temperatures are employed ranging from atmospheric temperature to around 60° C.; and particularly suitable are those within the range from 45° to 60° C.

The tertiary amine is employed in amounts ranging from around ¼% to 10% of the air-dry cellulose, and preferably in amounts of not more than 1%. Among tertiary amines suitable as catalysts in the process may be mentioned pyridine, 1-methyl pyrrol, tripropyl amine, triethyl amine, and trimethyl amine.

The vaporized tertiary amine may be introduced and contacted with the cellulose in several ways. For example, the autoclave containing the cellulose may be evacuated and the required amount of amine vapor allowed to flow in immediately prior to introduction of the alkylene oxide vapor; or the amine vapor may be contacted with the cellulose after contacting the latter with a small portion of the alkylene oxide vapor; or the two vaporous materials may be concurrently added slowly and proportionately to the cellulose. The first-named method is preferred. The amine vapor also may be passed through the cellulose and absorbed by the fibers up to the desired concentration prior to introduction of the alkylene oxide, although if the amine is absorbed by the cellulose to very large extent,—upon subsequent addition of the alkylene oxide, a portion of the latter is converted to aldehyde, which resinifies. This is particularly true when employing trimethyl amine.

The cellulose employed may be any of th usual commercial types. It is also possible to employ in the process neutral cellulose that has been previously depolymerized by treatment with mineral acid or the equivalent; and cellulose derivatives such as partially etherified or esterified celluloses which have some free hydroxyl groups.

In the preferred practice of the invention the cellulose material, such as cotton linters, which material preferably is in a highly fluffed state, is agitated or tumbled in a rotating jacketed autoclave which has been evacuated to remove the air. The alkylene oxide vapor is fed continuously into the rotating autoclave,—the flow thereof being adjusted to regulate the rate of the reaction and control the fluid presure within the autoclave. The catalysts may be introduced into the cellulose material either before or during flow of the alkylene oxide. The absence of appreciable dilution of the alkylene oxide vapor with air in the autoclave facilitates the hydroxyalkylation of the cellulose and prevents appreciable formation of oxycellulose in the presence of the catalyst. The rate of addition of the alkylene oxide vapor to the cellulosic material is regulated by a valve to approximately the rate at which it reacts with the cellulose material,—and so that the pressure within the autoclave never substantially exceeds that of the atmosphere. As a result of this slow addition of the alkylene oxide, it has been found that, when ethylene oxide is used as the hydroxyalkylating agent, the maximum amount of ethylene oxide vapor present at any time in the autoclave under atmospheric pressure at 50° C. is around 3% of the weight of the air-dry cellulose. In operations at lower pressures, this proportion desirably is increased somewhat. The reaction is completed when all of the oxide vapor introduced has reacted with the cellulose, so that the subatmospheric pressure secured by the original evacuation of the autoclave is approximately reached again. The resultant mass of etherified cellulose then is removed, and may be stored in that condition, or may be readily purified by extraction with warm water, centrifuged and dried.

When a cellulose that has been suitably depolymerized by any of the usual methods is employed as starting material, the final product of the process, either with or without the above-mentioned purification, may be peptized with a dilute aqueous solution of caustic soda (such as a 5% to 10% solution thereof). Otherwise the products are not peptizable, since neither the etherification process nor the purification step permits substantial depolymerization of the cellulose.

The following examples serve to illustrate the invention:

Example 1

100 grams of fluffy alpha wood pulp containing approximately 6% of moisture were introduced into an autoclave having an inside volume of 11.1 liters. After evacuating the autoclave to an absolute pressure of 4 mm. of mercury, 24 grams of ethylene oxide vapor and 0.312 gram of trimethyl amine vapor were simultaneously introduced over a period of 10 to 12 hours while tumbling the autoclave and heating at 60° C. until a pressure of approximately 228.6 mm. of mercury absolute was obtained. The resultant etherified cellulose was removed and, after purification by extraction with warm water, yielded 114.7 grams of a uniformly etherified hydroxyethyl cellulose which was practically insoluble in caustic soda even upon freezing, but was acetylated by the dope method very much more readily than the original cellulose material used as starting material.

Example 2

100 grams of loosely-fluffed cotton linters were introduced into the autoclave described in Example 1. After evacuation of the autoclave, 2 grams of pyridine vapor were introduced during agitation. Thereafter, 30 grams of propylene oxide vapor were slowly introduced into the autoclave over a period of 15 hours, during agitation thereof, while maintaining the contents at around 60° C. The heating and agitation were continued until a pressure of approximately 500 mm. of mercury absolute was secured in the autoclave. The resultant product, after extraction with warm water, yielded 108.4 grams of hydroxypropyl cellulose containing 8.4% of combined propylene oxide, and having properties similar to the product of Example 1 as to insolubility in dilute caustic alkali solutions and reactivity with acetylating agents.

Example 3

420 grams of loosely-fluffed, air-dry, low-viscosity alpha wood pulp, previously depolymerized with dilute sulfuric acid, were placed in a 5-gallon tumbling autoclave, the latter evacuated to a pressure of about 500 mm. of mercury absolute, and a small portion (about 10%) of a total charge of 109 grams of ethylene oxide vapor was introduced therein. Thereafter, 5.68 grams of trimethyl amine vapor were introduced, following which the balance of the ethylene oxide vapor was slowly added over a period of 5 hours. After 11 hours of tumbling and heating at 50° C., the original pressure of 500 mm. of mercury absolute obtained by the evacuation was again attained, and the reaction discontinued. The resultant etherification product was slightly pink in color, and showed a gain of 26.9% based upon the weight of the original alpha pulp.

It was substantially completely soluble in a dilute aqueous solution of caustic alkali yielding a solution well adapted for the preparation of films and filaments. This product also may be esterified, or may be ethylated, methylated or otherwise etherified to yield products well adapted for use in coating and impregnating compositions and in plastic compositions.

Example 4

Following the procedure described in Example 2, 1 gram of triethyl amine was introduced into a tumbling autoclave and mixed with 100 grams of alpha wood pulp. After securing in the autoclave a vacuum of 711.2 mm. of mercury absolute at 30° C., 20 grams of ethylene oxide vapors then were introduced over a period of 24 hours, during agitation of the mixture and while maintaining the same at around 60° C. At the end of 20 hours the autoclave pressure had fallen to 330.2 mm. of mercury absolute at the latter temperature. The resultant reaction product, hydroxyethyl cellulose, contained 4.3 grams of combined ethylene oxide based upon the original weight of the alpha pulp. It was substantially insoluble in dilute caustic alkali solutions, but is acetylated more readily than the alpha pulp starting material.

Example 5

To 55.3 grams of fibrous hydroxyethyl cellulose acetate, containing 23.6% of combined acetic acid and around 0.5% to 1% of moisture, was added water in amount sufficient to bring the moisture content of the mixture to approximately 8%. (The said hydroxyethyl cellulose acetate was prepared by reacting cotton linters with 15% of its weight of ethylene oxide, followed by acetylation of the resultant hydroxyethyl cellulose ether at 20° to 25° C., with an excess of acetic anhydride in the presence of sulfuric acid, using isopropyl acetate as a diluent. The aforesaid fibrous hydroxyethyl cellulose was removed from the acetylating mixture at the end of 4 hours purposely so as to obtain only a partially acetylated product.)

The diluted ester was placed in a 5-gallon container which was then evacuated. Thereupon 3.5 grams of pyridine were vaporized and conducted into the container and mixed with the diluted ester. 13.5 grams of ethylene oxide vapor were then slowly flowed into the container and the contents of the latter were agitated at 30° C. for 24 hours. The resultant product was thoroughly extracted with water to remove the pyridine and excess ethylene oxide. The washed product after drying at 70° C. for 24 hours weighed 59.9 grams and had a combined acetic acid content of 13.7%.

The practice of the present invention offers important advantages in instances where it is impracticable or undesirable to hydroxyalkylate cellulose in the presence of some carrier for the hydroxyalkylating agent or catalyst, such as water or a liquid organic diluent. The absence of diluents permits a more rapid and uniform reaction between the alkylene oxide and cellulose, and minimizes the amount of catalyst necessary to permit completion of the reaction under the mild hydroxyalkylating conditions. This obviates, too, the necessity for recovery of a liquid carrier. Purification of the final product is not necessary in most instances, as the amount of catalyst present is extremely small; and the mildness of the treatment prevents or minimizes the formation of any substantial amounts of undesirable cellulose depolymerization products. The readiness with which the etherified celluloses of the present invention may be purified is note-

worthy. Because of the low alkylene oxide content of the products, made possible by the use of small amounts of alkylene oxide, uniform products are readily obtainable which are less water-absorbent than products of the usual high alkylene oxide content, and which yield films having higher wet strengths than the latter. The use of low reaction temperatures within the temperature range named inhibits or prevents polymerization losses of the alkylene oxide and improves the efficiency of the process.

The term "a cellulose" is employed in the claims to designate not only more or less pure celluloses such as alpha wood pulp, sulfite wood pulp (rayon grades), cotton linters and the like, but also cellulose derivatives such as partially etherified or esterified celluloses having therein one or more free hydroxyl groups.

The invention is susceptible of modification within the scope of the appended claims.

I claim:

1. Process for the hydroxyalkylation of a cellulose, which comprises contacting a stream of vapors of an alkylene oxide with a cellulose, in the presence of a tertiary amine catalyst in the vapor-phase within a zone under subatmospheric pressure, and regulating the rate of introduction of the alkylene oxide to the said cellulose in accordance with the rate of reaction between said cellulose and said alkylene oxide, to prevent the pressure in the said zone from rising substantially above atmospheric pressure.

2. Process for the hydroxyalkylation of a cellulose which comprises slowly introducing a stream of vapors of an alkylene oxide into a cellulose within a zone under subatmospheric pressure maintained at a temperature within the range from around atmospheric to around 60° C., in the presence of vapors of a tertiary amine catalyst, regulating the rate of introduction of the alkylene oxide to prevent the pressure in the said zone from rising substantially above around atmospheric pressure, the total amount of alkylene oxide introduced into the said zone being between 1% and 30% of the weight of the cellulose.

3. Process for the hydroxyalkylation of a cellulose, which comprises subjecting an agitated body of cellulose to a subatmospheric pressure, contacting the resultant cellulose with successive small portions of an alkylene oxide in the presence of vapors of a tertiary amine catalyst while maintaining the resultant mixture at a temperature between atmospheric and 60° C., the rate of introduction of the alkylene oxide into the cellulose being no higher than that at which it combines with the cellulose, and the total amount of alkylene oxide thus contacted being less than 30% of the weight of the cellulose, and recovering the hydroxyalkylated cellulose thus produced.

4. Process as defined in claim 3 wherein the alkylene oxide employed is ethylene oxide, and wherein the maximum amount of uncombined ethylene oxide in contact with the cellulose at any time constitutes a few percent of the weight of the latter.

AUBREY ERNEST BRODERICK.

CERTIFICATE OF CORRECTION.

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It is hereby certified that error appears in the printed specification of the above numbered patent requiring correction as follows: Page 1, second column, line 11, for "th" read the; line 26, for "presure" read pressure; line 47, for "increased" read decreased; and that the said Letters Patent should be read with this correction therein that the same may conform to the record of the case in the Patent Office.

Signed and sealed this 17th day of October, A. D. 1939.

Henry Van Arsdale,
Acting Commissioner of Patents.

(Seal)

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2. Process for the hydroxyalkylation of a cellulose which comprises slowly introducing a stream of vapors of an alkylene oxide into a cellulose within a zone under subatmospheric pressure maintained at a temperature within the range from around atmospheric to around 60° C., in the presence of vapors of a tertiary amine catalyst, regulating the rate of introduction of the alkylene oxide to prevent the pressure in the said zone from rising substantially above around atmospheric pressure, the total amount of alkylene oxide introduced into the said zone being between 1% and 30% of the weight of the cellulose.

3. Process for the hydroxyalkylation of a cellulose, which comprises subjecting an agitated body of cellulose to a subatmospheric pressure, contacting the resultant cellulose with successive small portions of an alkylene oxide in the presence of vapors of a tertiary amine catalyst while maintaining the resultant mixture at a temperature between atmospheric and 60° C., the rate of introduction of the alkylene oxide into the cellulose being no higher than that at which it combines with the cellulose, and the total amount of alkylene oxide thus contacted being less than 30% of the weight of the cellulose, and recovering the hydroxyalkylated cellulose thus produced.

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