June 26, 1962 W. BOLASKI ET AL 3,041,246

ENZYMATIC CONVERSION OF CELLULOSIC FIBERS

Filed Dec. 28, 1959 3 Sheets-Sheet 1

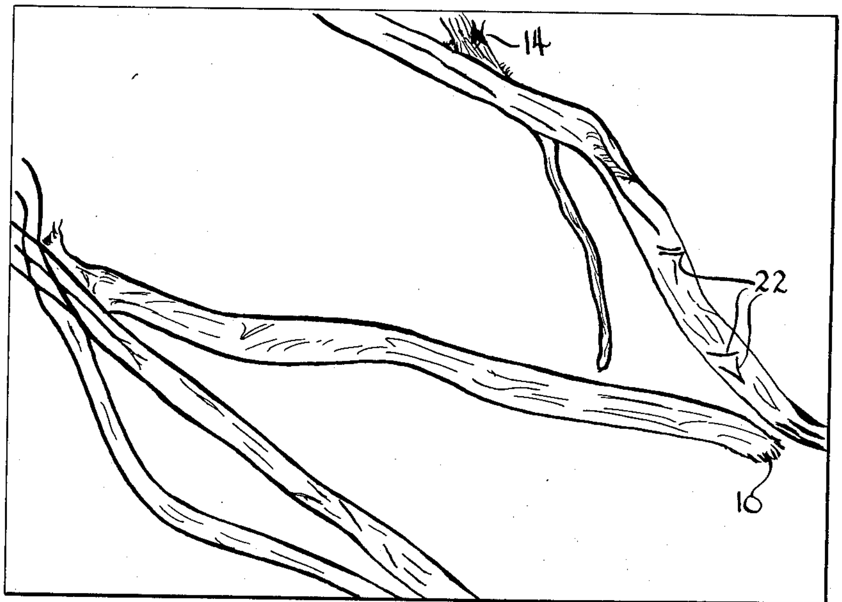

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Fig. 1.

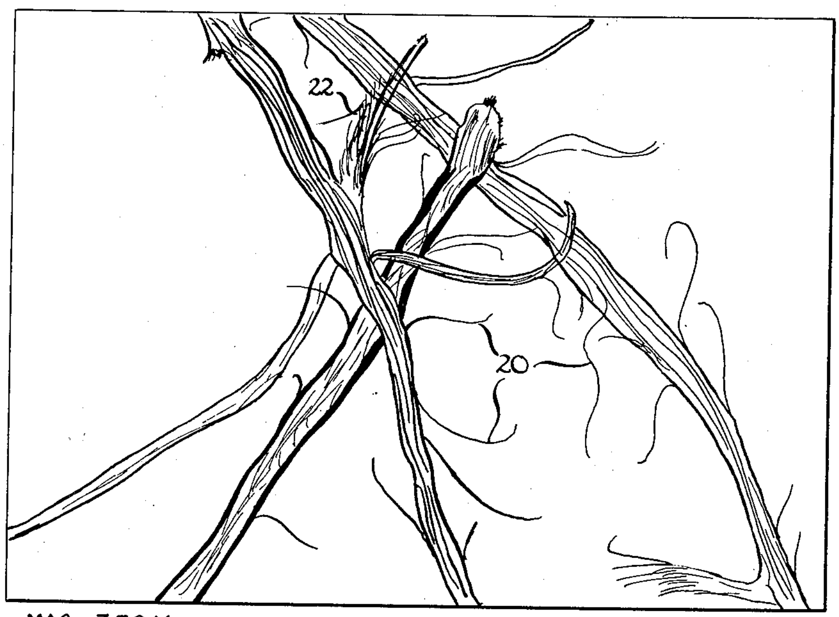

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Fig. 2.

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Fig. 3.

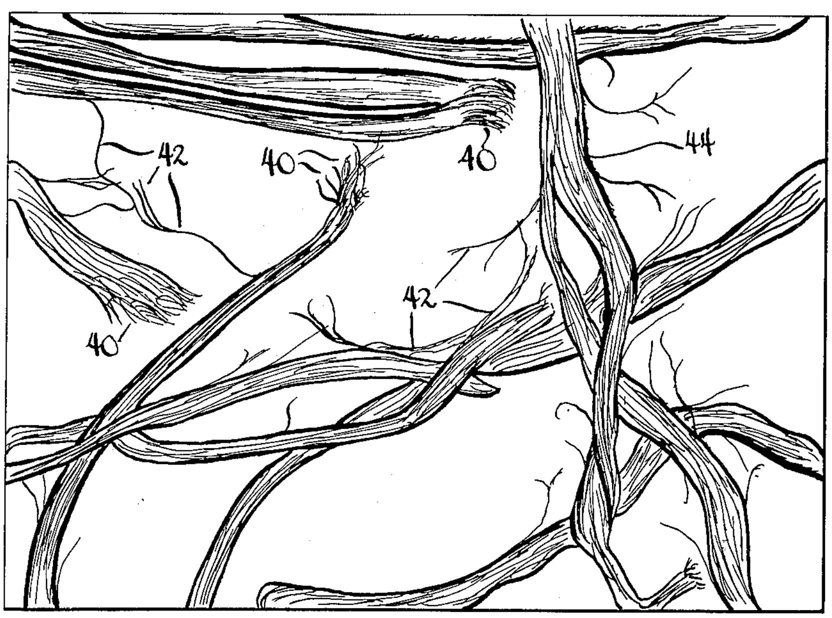

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Fig. 4.

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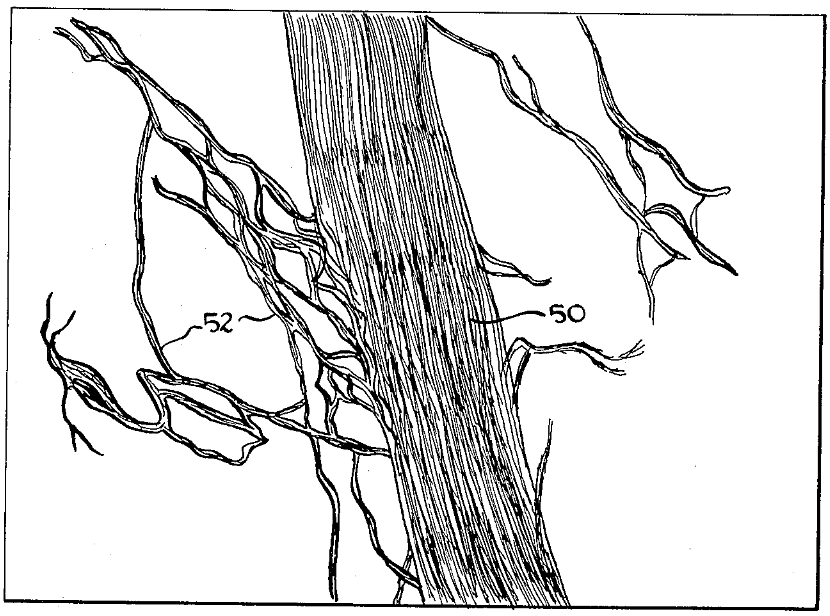

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Fig. 5

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ENZYMATIC CONVERSION OF CELLULOSIC FIBERS

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4 Claims. (Cl. 195—8)

The present invention relates to new and useful improvements in papermaking and is directed more particularly to a novel process for conditioning and enhancing the papermaking characteristics of cellulosic papermaking fibers, such as cotton linters or the like, by improving their fibrillation.

For purposes of definition, fibrillation, as employed herein, will be understood to mean the separating and rearranging of fibrils and/or segments of fibrils of a parent fiber.

It is generally appreciated that the strength of ordinary paper resides primarily in the bonds between the fibers. The intimate bringing together of fiber elements is necessary for the formation of strong bonds in paper. An increase in fibrillation, resulting from an increase in the conventional beating action, has promoted more extensive bonding between the fibers. As the degree of beating is extended, the strength of the paper attains a maximum value, beyond which increments in the degree of beating cause proportionate decreases in strength.

By the invention hereof, the fibers are so conditioned, through increased surface fibrillation, as to lead to an immeasurably improved degree of fiber contact resulting in a vastly greater number of potential bonding points in the process of making a paper web.

For optimum strength development a desideratum in fibrillation is to break down the fibers into fiber-like segments or fibrils of smaller diameter in such manner as not to create new surfaces to any appreciable extent and rather to expose already-existent surfaces in the cellulose upon the saturation thereof in a fluid.

The invention relates particularly to a novel enzymatic conversion of cellulosic papermaking fibers, such as unpurified or purified cotton linters, wherein the fibrils are separated or rearranged so that their functional characteristics are improved for subsequent conditioning and working.

More specifically, the invention comprises a method of or process for developing strength in such fibers by altering their condition through their conversion by enzymatic activity in order to obtain fibrillation without appreciable shortening of fibers in an economical and expeditious manner and the product of such method or process which possesses the desired strength characteristics and properties, all as exemplified in the detailed disclosure hereinafter set forth.

Stated otherwise, the invention contemplates a method of causing a concentration of enzymes, preferentially in the form of an aqueous dispersion or solution thereof, and prepared from one of the carbohydrolytic type enzymes, such as cellulase, to act on cellulosic fibers so as to produce fibrillation. It will be understood that the invention is adapted for use in fibrillating various cellulosic fibers, such as raw or purified cotton lint fibers, bast fibers, such as hemp, flax, manila, and the like, regenerated cellulose fibers, fibers derived from whole stems such as straw, esparto, bamboo and the like, and fibers derived from wood.

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Commercial methods of fibrillation have been heretofore developed but in most cases such methods have been exceedingly slow and laborious and the nature of the treatment has been often such as to impair the quality of the fiber and to produce a low yield, loss of fiber strength, decrease in length of fiber, and the like.

This invention envisions the manufacture of enzyme-treated cellulosic fibers and fibrous materials prepared therefrom, and is directed particularly to a method for improving the strength of felted fibrous cellulosic materials, such as paper and the like, by fiber alteration and fibrillation.

A salient object hereof is the provision of a method to control the degree of fiber alteration and fibrillation by controlling the enzymic action to a desired level, all depending upon the desideratum in the end product.

Another object of the invention is to provide a method offering an ability to produce paper by by-passing, or at least minimizing, the conventional processing and refining techniques in stock preparation.

A major role of fibrillation in producing strength is to provide greater surface tension forces having a capacity for drawing fiber surfaces into sufficiently close proximity for bonds to be established. With the increased fibrillation afforded by the invention hereof, the fiber flexibility and conformability of the surfaces is increased and hence surface tension forces during drying will produce more bondable areas.

The process of alteration envisioned herein is one which ensues under or in the presence of a liquid, a requisite for fiber swelling which is so all important in the ultimate development of strength in paper.

We employ a substantial excess of water with respect to the amount of fiber under treatment, the exact amount of water used being subject to considerable variation. In preferred practice, we employ a consistency of approximately 6% of fiber material.

Through the use of such a fluid, the swelling of the cellulose combined with the dimensional swelling of the fiber results in an opening up of the fiber structure.

The fluid penetrates the interfiber capillaries, and as the fiber swelling increases, the fiber structure is transformed into a more highly plasticized state wherefor fiber flexibility becomes greater and improved conformability of the fiber is made possible.

As conceived, this alteration or conversion is carried out to a degree where subsequent dispersion and minimum mechanical disintegration will expose the minute fibrils of the fibers and enhance their papermaking characteristics by increasing the potential for interfiber contact through the concomitant increase in the number of potential bonding points. The resulting fibrillar arrangement and/or rearrangement is such as to develop strength in cotton linter papers comparable to that exhibited by cotton lint fibers and/or cotton cutting papers.

Rag content paper manufacturers have recognized that the supply of good rag cuttings is dwindling, a condition brought about largely through the use of synthetic fibers as substitutes for, or replacements for, cotton fibers.

Looking toward the future, the time is foreseen when sufficient rags to meet the needs of the papermaker will not be available.

A new source of cellulosic fibers, suitable to papermakers' requirements, has been obviously essential for some time. The most promising source appears to be cotton linters because of their morphological similarity to cotton lint fiber. At the present time, cotton linters constitute more than 20% of the total cotton fiber used by rag paper mills. This fiber can be cooked and bleached so that it is satisfactory from the standpoint of the purity of the cellulose. Because the fiber is inherently stiffer, more wiry, and appreciably shorter than lint fibers, it does not provide strength comparable to that provided by good cotton rags.

Many efforts have been directed to improve the papermaking characteristics of cotton linters. Heretofore, the solution to the problem of obtaining improved strength in cotton linters has seemed to lie in chemical modification, ultrasonic disintegration, modification of present processes, modification in present equipment, or use of equipment of an entirely different type. These present methods are alike in that each process is variable and difficult to control and each is relatively slow in effecting fibrillation and developing strength in the cotton linter fiber.

From the economic standpoint, the cost of these processes or methods increases the cost of cotton linters, although performancewise, they appear to most persons skilled in the art to be somewhat superior to unmodified cotton linters.

Advantages hereof other than those described above will be apparent from the following description and claims taken together with the accompanying drawings wherein:

FIG. 1 is a diagrammatic plan view showing typical papermaking cotton linter fibers without any exposure to enzymatic action;

FIG. 2 is a diagrammatic plan view showing enzyme treated cotton linter fibers with a low order of fibrillation following a minimum of enzymatic action according to our invention;

FIGS. 3 and 4 are diagrammatic plan views showing enzyme treated cotton linter fibers with degrees of fibrillation greater than illustrated in FIG. 2 according to our invention; and

FIG. 5 is a diagrammatic plan view showing the extensive fibrillation of an enzyme treated cotton linter fiber according to our invention.

While, as above noted, our improved process involving enzyme-exposure is applicable to the fibrillation of fibers, and in particular cotton linters, it will be referred to specifically below as involving the following steps:

A preliminary treatment of the cotton linters will appreciably reduce the time and ease of subsequent treatment and may comprise a wetting operation for purposes of plasticizing the fibers and causing the amorphous areas thereof to swell.

The wetting has the capacity of extending the areas adjacent the cellulose molecules and to enlarge the broken ends, deep cracks, and abraded areas. This extension permits the enzyme to penetrate the fiber directly through the fiber wall and to separate and break the cellulosic chains to individual fibrils or groups of fibrils that adhere to the parent fiber.

An excess of solution is desirable, particularly where the operation is carried out on a large scale. This permits the maintenance of a more uniform concentration of treating solution at all points throughout the reacting vessel, and insures a uniform treatment of the fibrous material throughout the batch.

The concentration of enzymes of the carbohydrolytic type may be introduced to the liquid in the reacting vessel before or after the addition of the fibers.

Typical of the enzymes defined as of this genus is the cellulase enzyme.

The cellulase enzyme may be produced from a culture of *Aspergillus niger* and may be crystallized in one or several steps or stages of purification.

Insofar as purification is concerned, suffice to say that the more purified the enzyme, the less that is required for use. Contrariwise, the lesser the degree of purification, the greater the quantity required for use.

Enzymes are powerful catalysts with high reaction rates. Their reaction rate is instantaneous as of the moment they are contacted with the fibers assuming that all factors, hereinafter discussed, are at their proper levels.

The following gives one specific example to illustrate one method of producing the fibrillation of this invention, it being understood that other adjuvant materials may be similarly incorporated and that the quantities and types of substances added to the materials mentioned herein may be varied.

In the practice of our invention, water is heated to a temperature of 98.6° F. and is thoroughly mixed with a suitable acid, acid salt or salt capable of acid hydrolysis added in such quantity as to bring the water to the optimum hydrogen ion concentration corresponding to a pH of 4.0. At this point, it is desirable to stir the solution and introduce thereto 0.01%–2.0% of cellulase enzyme based on fiber weight and to add sufficient cotton linter fibers to obtain a consistency of from 3.0 to 8.0%. This mixture is maintained at the temperature noted above and mildly agitated within the reacting vessel throughout the enzymic conversion cycle.

A sufficient quantity of enzymes is preferentially employed to permit the solution intimately to contact all portions of the fiber material being treated and thereby insure the desired uniformity of penetration. In this connection, it has been found requisite to employ some agitation system by means of which the solution is carried into intimate contact with the fiber materials.

Without such stirring, which may be the equivalent of normal beater agitation, a localized action could result.

When the procedure thus outlined is followed, fibrillation of cotton linter fibers is noted in about ½ hour and continues to any desired degree until inactivated by one of various means, such as high temperature or the addition of chlorine.

It is known that factors affecting the activity of the enzymes includes: (1) time, (2) concentration, (3) temperature, (4) hydrogen ion concentration, and (5) activity of the particular enzyme employed.

Time

The amount of work accomplished is dependent upon the time of reaction.

It may be stated in general that the treatment for substantial fibrillation preparatory to papermaking may be accomplished in about ½ hour.

As an illustration, a 1% concentration of cellulase concentrate maintained at 98.6° F. temperature and a pH of 4.0 has produced desired fibrillation within a ½ hour reaction period for the fine writing and technical papers envisioned as being produced by the method hereof.

With a 5 hour reaction period, observable results have indicated that the reaction has exceeded optimum limits, some excessive disintegration of the fibers having taken place.

It will be appreciated, however, that for types of paper, other than the aforesaid fine writing papers, different reaction times may be more desirable.

Suffice to say that in the case of the above illustration, cotton linters so treated produced a pronounced degree of fibrillation as compared with untreated cotton linters agitated in the conventional manner during a like time period.

Concentration

The rate of attack upon the cotton linters is dependent upon the concentration of the enzyme employed. Generally speaking, where time is an important factor, the reaction rate may be increased by using enzymes in greater proportion. It is obviously primarily an economic consideration as to what the optimum operating conditions as to concentration are.

We have determined that a range of .01% to 2% (weight of enzyme to weight of fiber) may be employed.

By way of illustration, at the lower extreme of this range, .135 pound of enzymes may be added to 1350 pounds of cotton linters. At the higher extreme of this range, 27 pounds of enzymes may be added to 1350 pounds of cotton linters.

To go lower or higher and without the specified range would be economically impractical insofar as results are concerned.

Temperature

Enzymes are considered to be complex proteinaceous organic molecules and as such are sensitive to temperature.

The fibers are treated, according to the present invention, at temperatures in the range of 90° to 100° F. The reaction proceeds most rapidly in such range and preferably in the area of body heat, i. e. 98.6°.

At temperatures below 90° F., the reaction time required is sharply extended and, accordingly, it is preferable not to operate thereat, fibrillation not proceeding at an appreciable rate. Higher temperatures do not provide economical gains. Beyond 100° F., their activity decreases rapidly, and beyond 110° F., fibrillation does not proceed at an appreciable rate.

The particular temperature in the range of 90° to 100° F. is selected according to the particular material treated, the concentration of enzyme used, and the time of treatment.

At temperatures above 98.6° F., the time period of treatment is shortened at some sacrifice to fiber quality but the quality remains good up to 100° F.

Hydrogen Ion Concentration

Every enzyme has a pH range at which it is most effective and it usually loses most of this activity at a slightly different pH.

The enzymes hereof show their maximum activity at an acidic pH with optimum activity at a pH of 4.0. The resulting efficiency, when operating above pH 7.0, is such as to impair the activity of the enzymes.

Buffering agents, such as potassium acid phthalate or other salts and/or combinations thereof, may be added to the preparation in appropriate quantities to reduce the pH to the desired level and to maintain it thereat.

With specific reference now to the attached drawings, in FIG. 1, there is shown a groupment of typical cotton linter fibers, untreated according to the invention hereof. That is, this is a showing of fibers before alteration. The frayed end of a fiber is illustrated at **10**. The cracks within the fiber are illustrated at **12**. The abraded area, delineated by reference numeral **14**, shows an appreciable degree of fiber injury.

In FIG. 2, we have illustrated typical cotton linter fibers treated with the cellulase enzyme and showing the fiber swelling and surface fibrillation when compared with the fibers shown in FIG. 1.

The increase of exposed fiber surface area can be noted at **20**, same having been caused by the longitudinal separation or splitting off of the slender fibrils from the main body of the fiber. Initial liberation of fibrils is plainly visible, it being readily obvious that the tendency of the fibers is to split lengthwise into fibrils. Fibril agglomerates can be observed at **22**.

In FIGS. 3 and 4, a pronounced increase of fiber swelling and an increase of exposed fiber surface area is observable. The brooming or fraying of fiber ends is shown at **40** in FIG. 4. The increase of attached longitudinal fibrils of the fibers is shown at **42**, the very complete longitudinal splitting of the fibers being plainly seen.

Surface degradation as shown by the burred edge of the fiber is indicated at **34** in FIG. 3 and at **44** in FIG. 4.

The external surfaces of the fibrils provide the locations for potential interfiber bonding in the entanglement process of forming a paper web.

A sufficiency of fibrils for bonding back to the surfaces of the parent fiber, or of adjacent fibrils or to the surfaces of other parent fibers or fibrils thereof, is readily observable.

In FIG. 5, the arrangement of the fibrils within the cellulose fiber is illustrated at **50**. The longitudinal separation or splitting of the slender fibrils is shown at **52**.

Normally the fibrils are attached to the parent fiber. On occasion, some of the fibrils may be completely detached.

In FIG. 5 is clearly illustrated the ribbon-like arrangement of the fibrils or building units, as they are sometimes called, in the native cellulose fiber.

Since certain changes may be made in the above process and product and the specific example of the practice of the invention without departing from the scope of the invention herein involved, it is intended that all matter contained in the above description shall be interpreted as being merely illustrative and not as being limiting.

It is not intended thereby to have this invention limited to or circumscribed by the specific details of materials, proportions, or conditions herein specified, it being agreed that this invention may be modified according to individual preference or conditions without necessarily departing from the spirit of this disclosure and the scope of the subjoined claims.

Having thus described our invention and the best manner of practicing the new process for forming the novel composition thereof, all without limiting ourselves to the order of steps of such process recited, or to the proportions of parts employed therein, or to the precise ingredients named therein, as it is evident that each of these ingredients named therein has a considerable range of equivalents and as it is further evident that the order of steps and proportions of parts employed may be varied without departing from the scope and purpose hereof, what it is desired to claim and secure by Letters Patent of the United States is:

1. In the process of preparing a finished paper sheet, the improvement comprising, the altering of the papermaking fibers through the fibrillation thereof by a process which comprises treating the fibers in a bath of cellulase enzymes ranging in amount between 0.01% and 2.0% by weight to the weight of the cellulosic fibers treated and maintained at a temperature between 90° F. and 100° F. in a hydrogen ion concentration corresponding to a pH substantially at 4.0 during an enzymic conversion cycle not exceeding 5 hours.

2. In a method of preparing a paper sheet characterized by an increase in Mullen value, tear and fold, the improvement comprising, preparing sheet paper formed from an aqueous slurry formed with papermaking fibers altered through the fibrillation thereof by a process which comprises treating the fibers in a bath of cellulase enzymes, ranging between 0.01% and 2.0% by weight to the weight of the cellulosic fibers treated, the bath being maintained at a temperature between 90° F. and 100° F. and at a hydrogen ion concentration corresponding to a pH substantially at 4.0 during an enzymic conversion cycle not exceeding 5 hours.

3. In a process of making a finished paper sheet, an improvement in a biochemical process for conditioning the papermaking fibers comprising, the altering of the papermaking fibers through the fibrillation thereof by a process which comprises treating the fibers in an aqueous fibrillating bath of cellulase enzymes ranging in amount between 0.01% and 2.0% by weight to the weight of the cellulosic fibers treated and being maintained in the bath at a temperature between 90° F. and 100° F. and in a hydrogen ion concentration corresponding to a pH sub-

stantially at 4.0 during an enzymic conversion cycle not exceeding 5 hours.

4. In the process of making a finished paper sheet, the improvement in the controlling of the fibrillating of the cellulosic fibers by a process which comprises treating the fibers in a bath containing a concentration of cellulase enzymes in quantity for effectuating a partial reduction of the cellulosic fibers to filaments and having a consistency of from 3.0 to 8.0% and comprising 0.01% to 2.0% enzyme based on fiber weight and agitating same at a temperature of within the range of 90° F. and 100° F. and at a pH substantially of 4 during an enzymic conversion cycle not exceeding 5 hours.

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