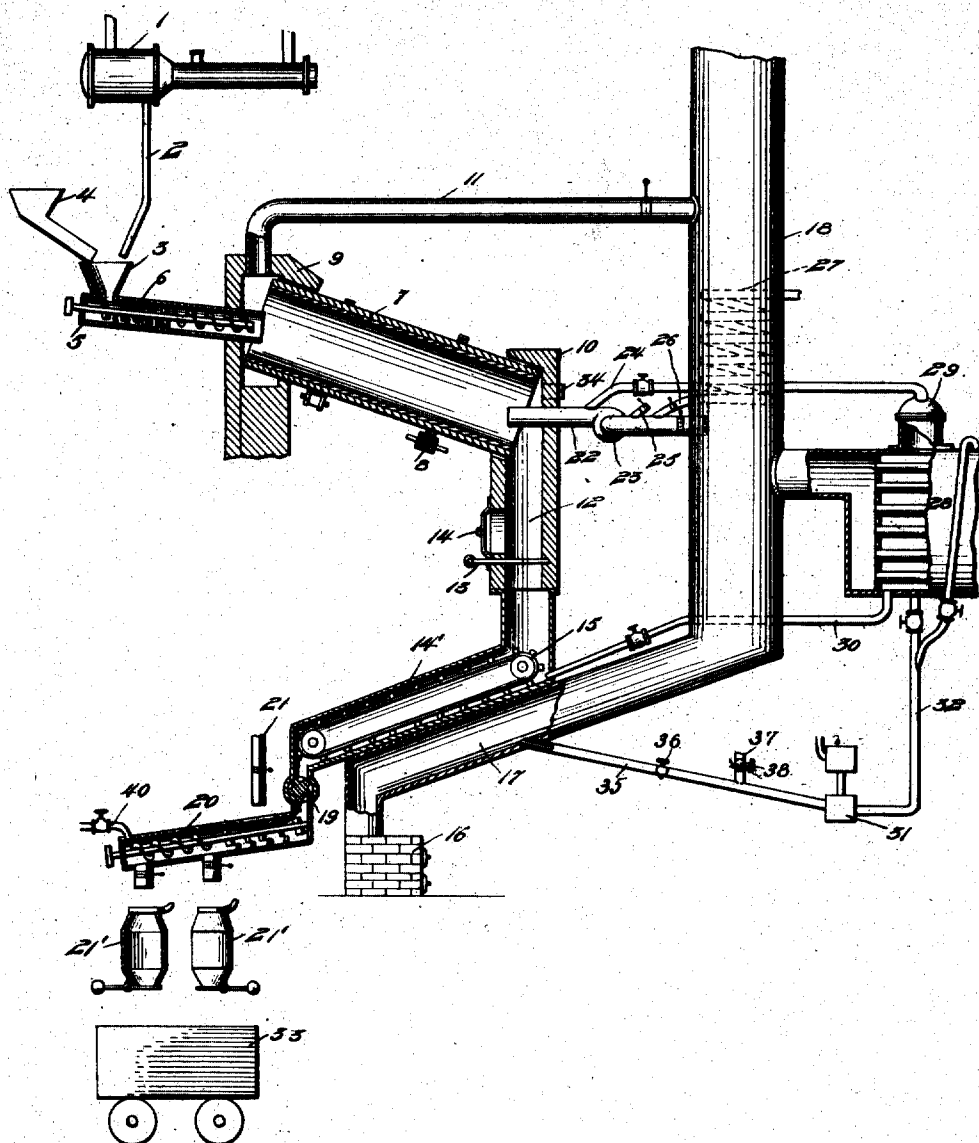


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 PROCESS OF MAKING ACETATES.
 APPLICATION FILED DEC. 29, 1908.

1,002,034.

Patented Aug. 29, 1911.



Witnesses

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33

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UNITED STATES PATENT OFFICE.

HARRY O. CHUTE, OF CLEVELAND, OHIO, AND KARL P. McELROY, OF WASHINGTON, DISTRICT OF COLUMBIA, ASSIGNORS TO LIGNO-CHEMICAL COMPANY, OF NEW YORK, N. Y. A CORPORATION OF NEW YORK.

PROCESS OF MAKING ACETATES.

1,002,034.

Specification of Letters Patent.

Patented Aug. 29, 1911.

Application filed December 29, 1906. Serial No. 350,011.

To all whom it may concern:

Be it known that we, HARRY O. CHUTE, a citizen of the United States, residing in the city of Cleveland, in the county of Cuyahoga and State of Ohio, and KARL P. McELROY, a citizen of the United States, residing in the city of Washington, in the District of Columbia, have invented certain new and useful Improvements in Processes of Making Acetates; and we do hereby declare the following to be a full, clear, and exact description of the same, such as will enable others skilled in the art to which it appertains to make and use the same.

This invention relates to processes of making acetates and consists in a method of preparing acetates from the products of the digestion of woody fibers with alkali by systematically and methodically heating such products under regulated conditions, and in recovering both the acetate formed and the excess of alkaline reagent; all as more fully hereinafter set forth and as claimed.

By heating wood, straw, and other natural fibrous materials with an alkali, one of the first results is a splitting of the natural molecules, or "compound celluloses", of the fiber to produce cellulose and another molecular group, or groups, uniting with the alkali to form soluble products. This is, of course, the basis of the ordinary soda pulp industry. By pushing the digestion further, as by use of longer digestion, more heat or more alkali, the yield of cellulose is lessened and that of these soluble by-products is increased. In general therefore in the soda pulp art, the digestion is pushed only to the point where a maximum yield of good clean cellulose results, these soluble by-products being ordinarily deemed absolutely worthless as such. It is indeed customary to concentrate the waste lye to a syrup, burn it and recover the soda by lixiviation as carbonate. In this liquid which in the art is termed waste soda lye among the soluble bodies is a large percentage of sodium acetate, a commercially valuable body, which, however, because of the extreme impurity of the solution cannot well be recovered, it being substantially impossible to crystallize it out. Acetate is contained in the soluble products made by digestion fiber with other alkalis and under other conditions than those obtaining in the soda pulp art, and certain

methods, particularly where some limited oxidation is allowed, result in larger yields of acetate. But, as stated, soda is the cheapest convenient alkali, and the waste lye of the soda pulp industry is the cheapest and most convenient form in which to obtain the acetate formed by its action on fiber. Such waste lye will hereinafter therefore be generally mentioned it being understood that other alkaline lyes from fiber may be used.

By pushing the heating of the alkaline lye and contained solubles further than was done in the digestion for cellulose, the amount of acetate is materially increased. A still further yield is obtained by permitting a limited oxidation. This is therefore done in the present process.

The syrupy soda lye as it leaves the usual vacuum evaporators is the raw material employed in the specific embodiment of the present process. The syrupy mass, however, it is practically impossible to heat methodically to the necessary regulated temperatures because of its physical consistency. On further heating in open vessels it passes gradually from a solution into a state of fusion of the contained soda salts, and it is impracticable to handle it with convenient apparatus, as it gums on stirring members and bakes on heating members, being thick, viscid and generally inconvenient. Further after reaching a certain degree of dehydration it is apt to ignite on heating as by contact with a spark or an overheated surface, burning away to charcoal and carbonate, and even when actual ignition does not take place, on exposure to free air it is very apt to take up an undue amount of oxygen, spontaneously rise in temperature and produce oxalates in lieu of the desired acetates, and especially in the presence of any potash. To produce maximum yields of acetate in it and to be able to extract this acetate, it is in general necessary to expose it for a time to a converting heat, best in the presence of a limited amount of available oxygen, between 100° and 200° C., and then to raise the heat to a point which will carbonize other matters than acetate; a temperature around 400°. In this latter operation, the danger of ignition is particularly great. After the converting and carbonizing operations, the material consists substantially of a mixture of sodium acetate, carbonate of soda and

char. This char however is in a finely subdivided form and in quite large amount, making the extraction of the acetate and carbonate rather difficult.

- 5 The converting operation may be performed upon the waste soda lye under heat and pressure in closed vessels, the advantageous amount of air being pumped into the vessel. The air so introduced is diluted by
10 the aqueous vapor generated from the lye itself to any desired extent and harmful oxidations can be altogether avoided. If the temperature be rather high, say 150° C., on removal from the boiler the water present
15 flashes into steam, and renders the lye, if sufficiently concentrated originally, of a consistency adapted to carbonization in any suitable apparatus. Another, and preferred method of effecting the conversion however
20 is to change the physical form of the lye by incorporating into it a solid, absorbent carrier, forming a sort of friable magma or solid, and then treat this mixture with diluted air, the dilution being of such extent
25 as to permit the acetate-forming oxidation without danger of ignition or undue oxidation.

In the preferred specific embodiment of my invention the syrupy soda waste lye
30 leaving the evaporators is reduced to a granular easily handled form by incorporating in it a granular carrier. Fine or dust-like solid material is not so good as offering difficulties in subsequent lixiviation. This carrier
35 should be substantially unaffected by the alkali, and should be insoluble. Charcoal braize, coke and iron ore are suitable materials. A certain amount of iron ore or manganese ore is indeed desirable as acting
40 catalytically in promoting the formation of acetate in some way not understood. This action may be due to alternate oxidations and reductions, or may not. Some little oxidation is desirable but this, as will subsequently
45 appear, may be easily afforded in other ways. However, the labile oxids, such as Fe_2O_3 and MnO_2 , are apparently desirable apart from their sheer oxidizing effect. The char obtained later on is frequently
50 suitable as an absorbent and has many advantages. The carrier employed should be in such amount and of such character as to convert the soda lye into a granular friable mass, either before or after drying.

- 55 Pure undiluted air should be excluded from the mass, while under treatment to prevent formation of oxalates and destruction of acetates. Atmospheres of various indifferent gases and mixtures may be employed, or even steam. As cheapest and
60 most convenient however, may be employed products of combustion, especially in the drying and in the preliminary or converting stage. Products of combustion ordinarily
65 carry a little oxygen; an amount insuffi-

cient for ignition or burning of the mass under treatment, but often still enough for the limited oxidation deemed desirable. They have the further advantage of quickly converting any caustic alkali present in the
70 lye into carbonate. Excess of caustic alkali tends to produce marsh gas from acetates by a well known reduction. As issuing from a boiler furnace, products of combustion have the additional advantage of being
75 about the right temperature for drying and converting the soda waste lye. From a well managed boiler furnace the waste gases leave at about 200° C.

The lye as absorbed in the pulverulent or
80 granular carrier may be first dried and then heated by direct exposure to gases from a boiler furnace, admixed with additional air or not as their composition may indicate, bringing it slowly up to a temperature be-
85 tween 110° and 200°; preferably with some pause at about 150° C. This results in a maximum production of acetate, that already present in the soda waste lye being reinforced in amount. This acetate, as
90 stated, however exists in the treated mixture in a very impure state, there being also soaps of higher fatty acids, soda salts of resins, waxes, and many other compounds. If
95 the mass be dissolved or leached with water after this treatment, while the acetate may be regained from the solution by crystallization or other means, such extraction is nevertheless difficult. The further, how-
100 ever, the oxidation is pushed in the conversion stage, the easier such extraction becomes. Therefore unless by-products are to be regained, which may be done by solution and fractional treatments of the material
105 after this operation, such material is preferably next carbonized. Acetate of sodium is a tolerably stable salt and stands temperatures up to 400° C., and perhaps somewhat
110 above, without much loss while the other organic bodies present are not so resistant, becoming carbonized at about 400° for the most part. If therefore the converted mass be next carbonized at or about these temperatures, a mass is obtained which consists
115 principally of sodium acetate and carbonate mixed with char and with the absorbent used. On leaching, which is best done by a methodically operating apparatus like the ordinary diffusion battery, the carbonate
120 and acetate are dissolved, leaving the char and absorbent behind. It is in this operation that a hard granular absorbent of the nature of coke is particularly useful as facilitating leaching. The natural char of the
125 carbonized mass while sometimes hard and resistant is oftener disintegrated in the leaching. Returned char used as an absorbent gives a harder char, better suited for leaching, however, than the char afforded
130 by leaching soda waste lye carbonized

50. A screened, granular coke, free from dust, may be used as an absorbent in the first treatment of lye, carried through the process to the leaching and then returned for re-use. Lighter, softer particles of carbon resulting from the charring of the lye itself can often be sifted away from the coke particles. A methodical burning will also remove them. However, the char formed upon coke sometimes has enough body to warrant its re-use. The siftings, elutriates or other char separated from the coke, where coke is used, or the excess char when char alone is returned, should ordinarily be burned to regain the soda carried. It is substantially impracticable and not particularly advantageous to leach to complete extraction of sodium salts, so that some is ordinarily left in the leached material. Separation of the acetate and carbonate in the leached solution may be effected by fractional crystallization.

There are several expedients which may be used in the recovery of the acetate with advantage when desired. One of these is to take the hot carbonized mass, prior to leaching, sprinkle it with water to cool and hydrate, and then subject to a current of cool products of combustion to convert the carbonate into bicarbonate. By then leaching with small amounts of water at ordinary temperatures, most of the bicarbonate is left behind in the char and the acetate solution formed is relatively pure. The bicarbonate can then be leached out with hot water, or the char burned to ash and the carbonate then leached.

Ordinarily, when operating with soda pulp lye, all the sodium carbonate regained in the various operations should be causticized and sent back to the pulp mill.

An advantageous method of operating is to leach the carbonized mass with hot water, extracting everything soluble. Hot water gives a tolerably concentrated solution and good extraction. From this solution, the acetate and carbonate may be directly separated by fractional crystallization in well understood ways. Or, the solution may be cooled, gassed with products of combustion to precipitate most of the carbonate as bicarbonate, and then fractional crystallization practiced. Mother liquors after crystallization may be burned to regain carbonate.

In the accompanying sheet of drawings is shown, rather diagrammatically, one form of apparatus of the many adapted to perform the described process.

In this illustration: 1 is an ordinary type of evaporator reducing soda waste lye, the bottom effect of a multiple effect being indicated. Thick lye leaves it through 2 and in hopper 3 meets granular absorbent from 4. From the hopper the mixture of lye and ab-

sorbent is delivered into a conduit 5, provided with a screw conveyer carrying breaking and mixing blades 6 at its upper end and a screw at its lower. This completes the mixture and perfects the absorption. From the conduit the mixture, which should be friable and granular, is sent into converting apparatus 7, which, as shown, consists of a rotary cylinder, driven by gear 8 and housed by end casings 9 and 10. The former is provided with a valved flue 11 leading to a stack. The latter is provided with a conduit 12 receiving material from the rotary converter and provided with a valve 13 and door 14 permitting removal of converted material prior to carbonization if so desired. Downwardly the conduit leads into a carbonizer, indicated as a whole by 14'. This carbonizer, as shown, is set at an angle and contains the drag conveyer 15. A furnace 16 sends heat through flue 17, thereby heating the carbonizer above said flue. The flue leads to stack 18. From the carbonizer the material is fed by gate 19 into conduit 20, also provided with a breaking conveyer. Pipe 21 allows wetting the material immediately upon exit from the carbonizer. From this conduit, the cooled material may be fed into either of the diagrammatically shown leachers 21'. Pipe 40 allows introduction of products of combustion.

To secure the necessary conditions, thermal and chemical, in the rotary converter, the latter is provided with a pipe 22 fed by blower 23 from the chimney stack and thereby adapted to introduce products of combustion in regulated amount. Connected to this pipe is a valved steam pipe 24. On the suction side of the fan is a valved inlet 25 permitting introduction of regulated amounts of cold air. Pipe 26, communicating with stack heater 27, permits introduction of heated air. Connecting with the stack is shown fragmentarily an ordinary boiler 28, provided with steam dome 29 and valved outlet pipe 30 leading into the carbonizer. Soda pulp waste lye may be boiled down in this boiler and led directly to the carbonizer. A high pressure pump 31 and pipe 32 permit introduction of a certain amount of air or air mixed with products of combustion into the boiler against the steam pressure to aid in oxidation, as described. Conduit 35 valved at 36 offers communication between the pump and a source of products of combustion. Air inlet 37 valved at 38 allows the use of any desired amount of air admixed with the products of combustion.

Car 33 is provided for the reception of leached material.

The operation of the apparatus shown is as follows: Using soda waste lye, it is taken up by an absorbent in the breaking and mixing conduit and fed in regulated amounts into the converter. Here it is exposed to

regulated heat and oxidation by the current of boiler gases. With the rotary converter shown, a greater or less speed of rotation corresponds to a greater or less forward progress of the material therethrough and control of the time of exposure to the heat is consequently afforded. Speed of feed of the screw conveyer is of course adjusted to correspond to the speed of the rotary converter.

As the materials enter damp, the heat in the converter at the upper end is not ordinarily much above 100° C. while at the lower end it reaches about 200° with boiler gases. By slow rotation and feed, the higher temperature is pushed backward toward the entrance and conversely. The heat of the boiler gases can be tempered as much as may be desired by the steam. For present purposes, both steam and boiler gases act alike, both diluting whatever air may be present. Boiler gases with ordinary firing usually contain as much excess air as is necessary, but with more careful firing, using less excess of air under the grate, it is frequently desirable to introduce a little hot or cold air. With careless firing, it is sometimes better to dilute the products of combustion further with some steam. For the present purpose of course, ordinary boiler gases may be deemed diluted air, being a mixture of more or less unchanged air with products of combustion.

It is usually desirable to run the greater part of the converter at an average temperature of about 150°. Thermometric observations may be made through the plugged orifice 34. A mixture of air and inert gases corresponding to 10 to 20 per cent. air is a suitable atmosphere to be used in the converter, the higher the average heat, the more dilute being the air. It is not necessary to run the converter with air tight housings, which adds to the convenience of the apparatus shown, but there should be a slight plenum therein to insure that leakage shall be outward. In the carbonizer the temperature at the lower end should not exceed 400° C. as a rule, though 10 or 20 degrees excess do no great harm. Oxidation is not necessary or desirable here and no gas introducing means are shown. Some gas is evolved in the carbonization and this provides a suitable atmosphere, being non-oxidizing. It escapes upward through the feed conduit and mixes harmlessly with the products of combustion.

The apparatus shown may be used to produce acetate directly from woody fibers without employing soda waste lye as a raw material. For this purpose, saw-dust, comminuted straw or the like may be soaked in alkali solution and introduced through hoppers 4 and 3 into the apparatus. Using this as a raw material, acetate is produced to a large extent at the expense of the cellu-

lose portion of the woody molecules, as well as at that of the "ligno-cellulose;" the portion extracted by soda in making soda pulp. With such fibers used directly, the fiber itself acts as an absorbent.

What we claim is:

1. In the manufacture of acetates, the process which consists in first producing an alkali solution of woody-fiber constituents, then absorbing the same in an absorbent material and oxidizing the mass while in a heated state by means of diluted air.

2. In the manufacture of acetates, the process which consists in producing an alkali solution of woody-fiber constituents, absorbing the same in an absorbent material and oxidizing the mass while in a heated state by means of air diluted with products of combustion.

3. In the manufacture of acetates, the process which consists in producing an alkali solution of woody-fiber constituents, absorbing the same in an absorbent material, oxidizing the mass while in a heated state by diluted air and carbonizing by a higher heat out of contact with air.

4. In the manufacture of acetates, the process which consists in producing an alkali solution of woody-fiber constituents, absorbing the same in an absorbent material, oxidizing the mass while in a heated state by diluted air, carbonizing by a higher heat out of contact with air, and separating the carbonate and acetate of alkali from the carbonized mass.

5. In the manufacture of acetates, the process which consists in passing a granulated mass of alkalized woody-fiber constituents past a current of hot diluted air, traveling in the opposite direction, the temperature of said diluted air and the amount of oxygen therein being controlled to cause formation of acetates.

6. In the manufacture of acetates, the process which consists in absorbing an alkaline solution of woody-fiber constituents in an absorbent to produce a granular mass and passing said granular mass past a current of hot diluted air, traveling in the opposite direction, the temperature of said diluted air and the amount of oxygen therein being controlled to cause formation of acetates.

7. In the manufacture of acetates, the process which consists in absorbing an alkaline solution of woody-fiber constituents in an absorbent to produce a granular mass, passing said granular mass past a current of hot diluted air and carbonizing by a higher heat out of contact with air.

8. In the manufacture of acetates, the process which consists in mixing waste soda pulp lye with a granular absorbent to produce a granular mass, and passing said granular mass past a current of hot diluted

air, traveling in the opposite direction, the temperature of said diluted air and the amount of oxygen therein being controlled to cause formation of acetates.

5 9. In the manufacture of acetates, the process which consists in mixing waste soda pulp lye with a granular absorbent to produce a granular mass, passing said granular mass past a current of hot diluted air
0 and carbonizing out of contact with air.

10. In the manufacture of acetates, the process which consists in mixing waste soda pulp lye with a granular absorbent to produce a granular mass, passing said granular
15 mass through a rotary cylinder while in contact with a heated atmosphere containing products of combustion and air, and carbonizing out of contact with air.

20 11. In the manufacture of acetates, the process which consists in mixing waste soda pulp lye with a granular absorbent to produce a granular mass, heating said mass to produce acetates and carbonizing the mass in the neighborhood of 400° C.

25 12. In the manufacture of acetates, the process which consists in oxidizing heated woody-fiber constituents combined with al-

kali by means of diluted air and then carbonizing out of contact with air.

13. In the manufacture of acetates, the
30 process which consists in oxidizing heated soda waste lye by diluted air and then passing the oxidized material continuously down a heated conduit out of contact with external air.

14. In the manufacture of acetates, the
35 process which consists in drying and heating soda waste lye to an acetate forming temperature out of contact with pure air and in then carbonizing out of contact with
40 air.

15. In the manufacture of acetates, the process which comprises absorbing soda waste lye in an absorbent material and sub-
45 jecting the mass to the oxidizing action of diluted air at acetate forming temperatures.

In testimony whereof we affix our signatures in the presence of two witnesses.

H. O. CHUTE.
K. P. McELROY.

Witnesses:

C. W. FOWLER,
ALFRED M. HOUGHTON.