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METHOD AND APPARATUS FOR DETERMINING CRYSTALLIZATION POINT

Filed July 31, 1962

FIG. 1

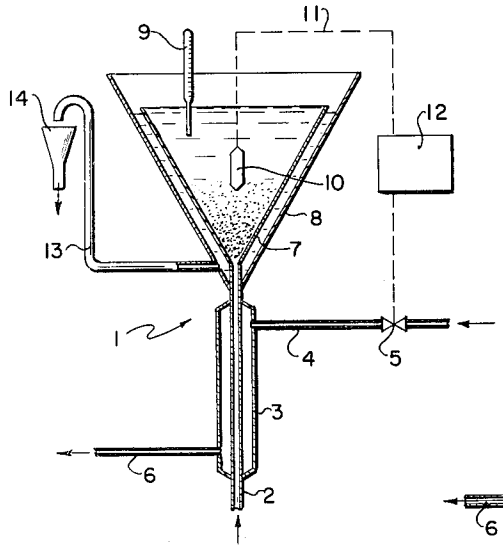


FIG. 2

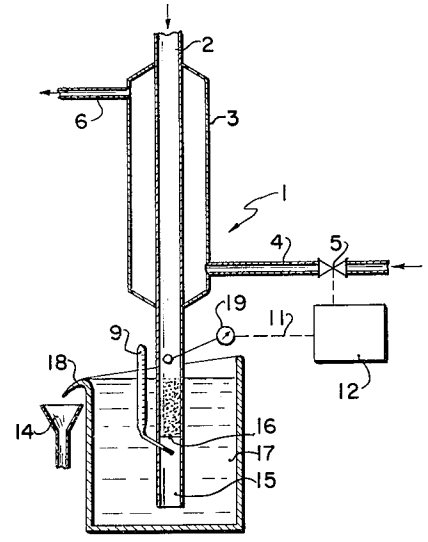
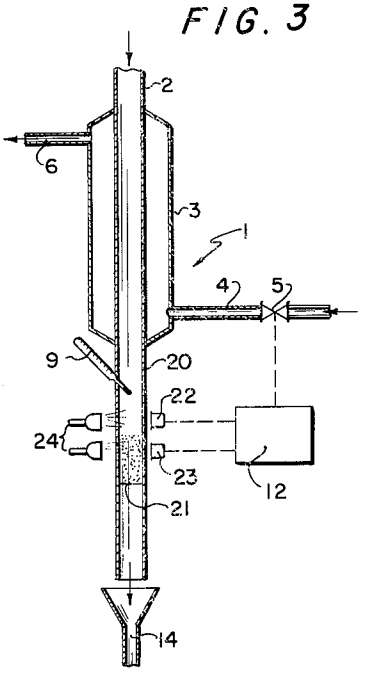


FIG. 3



INVENTOR.
LEENDERT VAN ASSENDELFT

BY Robert W. Hahl

ATTORNEY

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METHOD AND APPARATUS FOR DETERMINING CRYSTALLIZATION POINT

Leendert van Assendelft, Arnhem, Netherlands, assignor to American Enka Corporation, Enka, N.C., a corporation of Delaware

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8 Claims. (Cl. 73—17)

This invention relates generally to spin bath solutions used in the viscose process and more particularly to a method and apparatus for continuously determining the crystallization point of sodium sulfate in such spin baths whereby the components of the bath solution can be continuously held constant.

It is known that the sodium sulfate content of spin baths used in the viscose process can be determined by density measurement. Since the density of the spin bath increases with the sodium sulfate content, the values found for the density are indicative of the sodium sulfate content. However, the results obtained by this measuring method are not accurate, since the sulfuric acid and the other salts present, such as zinc sulfate and magnesium sulfate, also influence the density of the bath. Thus, fluctuations in the contents of such compounds strongly influence the measuring results.

Therefore, it is an object of this invention to provide a method for continuously determining the sodium sulfate content in viscose spin baths not having the disadvantages inherent in the known method.

Another object of this invention is to provide a method for accurately determining the sodium sulfate content in viscose spin baths.

Still another object of this invention is to provide a method and apparatus for continuously determining the crystallization point of sodium sulfate in viscose spin baths.

A further object of this invention is to provide a method and apparatus for accurately determining the crystallization point of sodium sulfate in viscose spin baths which is not influenced by fluctuations in content of other components present in the bath.

These and other objects are accomplished in accordance with this invention by separately and continuously determining the crystallization point of the sodium sulfate in the bath and the sulfuric acid content thereof. The sodium sulfate content is then continuously derived from the thus determined crystallization point and the sulfuric acid content. In carrying out the method of this invention, use is made of the fact that the sulfuric acid content, the sodium sulfate content, and the crystallization point of the spin bath are so related that upon determining two of these quantities, the third can then be derived. Consequently, if in a given spin bath two of these quantities are known, the third may be determined therefrom. By the method of this invention, the sodium sulfate content is derived from the sulfuric acid content, and the crystallization point, both of which are determined in a continuous manner. The sodium sulfate content can then be derived from the values found with the aid of a graph or nomograph. However, for practical reasons, it is preferred to employ automatic control equipment which converts the data received from the apparatus used in measuring the crystallization point and the sulfuric acid content into data which directly indicates the sodium sulfate content. The latter data is then used to control correction apparatus which maintains a constant sodium sulfate content. Since the data received from the continuous titration of the sulfuric acid can nearly always be used for controlling the correction stream of

the sulfuric acid, the spin bath entering the measuring apparatus will have a constant sulfuric acid content. The crystallization point of the bath is then only dependent on the sodium sulfate concentration. Thus the sodium sulfate content may be derived directly from the crystallization point, since the sulfuric acid content always has the same value.

Other salts present in a spinning bath, such as zinc sulfate and magnesium sulfate, have very little influence on the determination of the sodium sulfate content. The presence of these salts may be considered when interpreting the results obtained. However, the influence of fluctuations in the concentrations of these salts on the crystallization point of the bath is negligible.

Conventional measuring apparatus for continuously determining the sulfuric acid content can be used, the acidity being determined by titrating a continuous stream of liquid, for example a sodium hydroxide solution, with a continuous stream of the bath to be examined.

The crystallization point can be determined in various ways. In principle, the determination is carried out by cooling a stream of the spin bath and measuring the temperature at which crystallization occurs. For example, the spin bath is cooled and then passed through a layer of glauber salt crystals. The cooling is so controlled that none of the glauber salt crystals are dissolved and none precipitate from the bath. Very accurate and reliable apparatus that may be used for this purpose, which continuously measures the crystallization point, comprises a flow channel surrounded by a cooling jacket provided with an adjustable inlet for introducing cooling liquid thereto. The flow channel opens in a crystallization chamber provided with discharge means. A thermometer and a sediment level indicator controlling the inlet for the cooling liquid through a control device are disposed within the crystallization chamber.

In one embodiment the apparatus is so constructed that the crystallization chamber comprises a funnel-shaped, downwardly tapering vessel, the upper edge of which forms the discharge means. The flow channel is connected at the bottom of the chamber with the sediment level indicator being an immersion body freely adapted to move both in an upward and downward direction. The immersion body used is of a type that will sink in the liquid being examined but will float on the layer of crystals.

In such an apparatus the spin bath liquid enters the flow channel, where it is cooled until the sodium sulfate crystallizes out of solution, the crystals forming a layer in the bottom of the crystallization chamber. As the layer of crystals increases, the immersion body is raised so that the control device connected therewith causes the inlet opening for the cooling liquid to constrict. As a result, the spin bath stream is cooled to a less degree. This continues until the liquid passing through the layer of sodium sulfate crystals is no longer saturated so that some of the sodium sulfate goes back into solution. The immersion body will then descend, thus slightly enlarging the inlet opening for the cooling liquid, as a result of which the spin bath stream is cooled again slightly. Consequently, the amount of cooling liquid is controlled by the immersion body so that a solution which is just saturated with sodium sulfate continuously enters the crystallization chamber at a temperature close to the crystallization point.

The temperature is read from the thermometer present in the chamber and is a measure of the amount of sodium sulfate in the spin bath. By means of this reading, the apparatus controlling the sodium sulfate content in the bath may be adjusted. In practice, a so-called control thermometer is used which regulates the apparatus correcting the sodium sulfate content through a conventional

control device. For example, a thermometer is used which closes an electric circuit when the crystallization temperature deviates a given fraction from the desired crystallization temperature. The resulting signal is then used by way of conventional apparatus to increase or decrease the stream of spin bath being passed through the crystallizer, depending on whether the crystallization temperature is either too high or too low.

In another very satisfactory embodiment, the apparatus is constructed so that the crystallization chamber contains a partition permeable to liquids but impermeable to crystals. The partition divides the chamber into two parts, the flow channel being connected to one part, and the discharge member to the other. In such an apparatus, the layer of sodium sulfate crystals forms on the partition. The sediment level indicator of this apparatus is preferably a pressure meter which measures the pressure drop in the liquid through the layer of crystals. The pressure drop increases as the layer of crystals becomes thicker. It is also possible to use a combination of two light sources and two photo-electric cells such that the layer of crystals forms between the light sources and the photo-electric cells. They are arranged so that one photo cell receives light while the other does not when the layer of crystals has the correct depth. When the depth of the layer increases, the beam of light received by one photo-electric cell is interrupted, as a result of which the stream of cooling liquid is reduced. When the thickness of the layer decreases, the cell which first received no light now receives light, as a result of which the stream of cooling liquid is increased.

The crystallization point can also be determined through use of the heat released upon crystallization or the sudden drop in electrical conductivity upon crystallization. However, the simplest apparatus is that in which the cooling of the bath stream is so controlled that the bath is in equilibrium with the sodium sulfate crystals.

For purposes of illustration, there are shown in the drawings several embodiments of the apparatus according to this invention. However, the invention is not intended to be limited to the precise instrumentalities and arrangements shown.

FIGURES 1, 2, and 3 are vertical views in section showing three embodiments of the apparatus for cooling a spin bath stream down to its crystallization point. The cooling is then adjusted by a control device which is regulated by apparatus measuring the depth of sodium sulfate crystals through which the cooled spin bath stream passes.

In FIGURE 1 the apparatus for the determination of the crystallization point designated generally at **1** comprises a vertical conduit **2** surrounded by a cooling jacket **3** provided with a supply line **4** and a control valve **5**. Cooling liquid flows into cooling jacket **3** through supply line **4** and is discharged through line **6**.

Vertical conduit **2** opens in the lower end of funnel-shaped vessel **7** surrounded by a second funnel-shaped outer vessel **8**. In vessel **7** a thermometer **9** and an immersion type sediment level indicator **10** are positioned. Sediment level indicator **10** is connected by line **11** with control device **12** which adjusts the opening of control valve **5**. A discharge line **13** connected at the base of outer vessel **8** opens into collector **14**.

In using the apparatus, sodium sulfate crystals are placed in vessel **7**. The liquid spin bath enters the apparatus at the lower end of conduit **2**. In conduit **2** the bath is cooled down to its crystallization point. The feed rate of the spin bath is controlled so that the force of gravity does not cause the crystals in the vessel **7** to enter conduit **2**. When the amount of cooling liquid entering cooling jacket **3**, by way of the line **4**, is such that the liquid spin bath on entering vessel **7** has assumed the temperature of the crystallization point, no sodium sulfate will dissolve from the crystal layer or precipitate from the bath. However, if the temperature of the spin bath is somewhat higher than the crystallization point, sodium sulfate will go into solution. As a result, sediment level indicator **10** will move downward, thus increasing, by way of the control device, the opening of control valve **5**. The amount of cooling liquid entering the cooling jacket **3** will increase, so that the temperature of the spin bath entering the vessel **7** will fall. When the temperature of the spin bath falls below the crystallization point, sodium sulfate will precipitate from the spin bath, so that the layer of crystals present in vessel **7** will increase, thus resulting in the control valve opening being reduced. The temperature of the spin bath at the thermometer **9** deviates only slightly from the crystallization point. The spin bath leaves the vessel **7** by way of the space between the vessel **7** and the outer vessel **8** through the acid discharge line **13**, thus preventing the occurrence of undesirable variations in temperature in the vessel **7** due to the exchange of heat with the surrounding apparatus.

The reading on thermometer **9**, in combination with the sulfuric acid content, which is determined conventionally, is a measure of the sodium sulfate concentration. This concentration may be determined, for example, with the aid of a graph or a nomograph.

In FIGURE 2, numerals **1**, **2**, **3**, **4**, **5**, **6**, **9**, **11**, **12**, and **14** refer to parts having the same function as in FIGURE 1. Near outlet **15** the conduit **2** is divided into two parts by a piece of fiber glass fabric **16**. Outlet **15** ends in a vessel **17** which is provided with an overflow **18**. Above the piece of fiber glass fabric **16** there is a pressure meter **19** which is connected with control valve **5** by way of the line **11** and the control device **12**. Below the fabric **16** is positioned a thermometer **9**.

When using the apparatus, an increase or decrease in the amount of sodium sulfate crystals results in an increase or decrease in pressure in the liquid over the fabric **16**. These variations in pressure are communicated to the control valve **5** by way of the pressure meter **19** and control device **12**. Thermometer **9** always indicates a temperature which deviates only slightly from the crystallization point of the bath liquid.

In FIGURE 3, numerals **1**, **2**, **3**, **4**, **5**, **6**, **9**, **12**, and **14** refer to parts having the same function as in FIGURES 1 and 2. Section **20** of conduit **2** is of glass. A partition **21** and fiber glass fabric is positioned in section **20** on which a layer of crystals may precipitate. The height of this crystal layer is measured by photo cells **22** and **23** which are activated by light source **24**. Photo cells **22** and **23** are connected with control device **12** so that said control device increases the opening of control valve **5** when photo cell **23** receives light as a result of a decrease in depth of the crystal layer, and narrows the opening when photo cell **22** receives no light as a result of an increase in depth of the crystal layer.

Using the method of this invention, it is now possible to accurately determine the sodium sulfate content of a circulating spin bath and keep the sodium sulfate content constant within very narrow limits by means of the measured values. As a result, spinning conditions can be kept more constant than heretofore thought possible. Not only will this lead to a more uniform yarn, but use may be made of spinning processes which are very critical regarding the sodium sulfate concentrations without there being any risk of inadmissable variations in this concentration. If the sodium sulfate content is automatically controlled and at the same time the sulfuric acid content is controlled, an additional advantage results in that the zinc sulfate content may be determined in a simple manner by density measurement, since the only remaining factor controlling the density of the spin bath is the zinc sulfate, provided there are no other salts present that would affect the density. Thus by continuously measuring the density in a conventional manner and using the measuring apparatus of this invention, it is possible to automatically control the sulfuric acid, sodium sulfate, and zinc sulfate contents very accurate and in a continuous manner.

The invention is further illustrated by the following example.

Example

The crystallization points of four different spin baths, *a*, *b*, *c*, and *d* were determined with the apparatus shown in FIGURE 1. By means of titration the sulfuric acid content was also determined. From the values obtained the sodium sulfate content was determined with the aid of a graph. The density of the liquids and the sodium sulfate and zinc sulfate contents were then determined by conventional methods known in chemical analysis. The values obtained are summarized in the table below.

Table

Spin bath	*a*	*b*	*c*	*d*
1. Sulfuric acid content determined by titration, percent by wt.	6.50	6.50	6.50	6.50
2. Measured crystallization point, °C.	11.1	11.1	12.2	12.2
3. Sodium sulfate content derived from 1 and 2, percent by wt.	14.0	14.0	15.0	15.0
4. Density	1.225	1.237	1.235	1.247
5. Sodium sulfate content, percent by wt.	14.0	14.0	15.0	15.0
6. Zinc sulfate content, percent by wt.	3.0	4.0	3.0	4.0

The table clearly shows that it is possible in accordance with the invention to accurately determine the sodium sulfate content and that a varying zinc sulfate content does not influence the results. With the method of the prior art in which sodium sulfate content is determined by density measurements, variations in zinc sulfate content influence the results considerably, since zinc sulfate contributes to the density of the spin bath in the same magnitude as sodium sulfate.

While the invention has been described in connection with the foregoing drawings and examples, many changes, embodiments, and modifications within the scope of the invention will be apparent to those skilled in the art. Accordingly, the invention is intended to be limited only as set forth in the following claims.

What is claimed is:

1. Apparatus for continuously determining the crystallization point of circulating solution comprising a conduit for carrying said solution, a cooling jacket surrounding said conduit provided with liquid inlet and outlet means, said inlet means being adjustable for controlling the flow of cooling liquid into said cooling jacket, a crystallization chamber connected to said conduit for receiving solution therefrom, solution discharge means connected with said chamber, a sediment level indicator positioned in said chamber for indicating a surface level of crystals deposted therein, means connected to said sediment level indicator for adjusting said inlet means to maintain said level substantially constant, and a thermometer positioned within said chamber for continuously determining the crystallization point of said solution.

2. The apparatus of claim 1 in which the crystallization chamber comprises a funnel shaped vessel connected with said conduit at the apex of said funnel-shaped vessel.

3. The apparatus of claim 1 in which the crystallization chamber contains a partition permeable to the solution but impermeable to crystals whereby crystals collect on said partition and the solution passes therethrough.

4. The apparatus of claim 1 in which the sediment level indicator is an immersion body adapted to move freely in a vertical direction.

5. The apparatus of claim 1 in which the sediment level indicator is a pressure meter.

6. Apparatus of claim 1 in which the sediment level indicator comprises two light sources and two photoelectric cells adapted to respond according to the crystal depth.

7. Apparatus for continuously determining the crystallization point of a circulating spin bath solution used in the viscose process comprising a conduit for carrying a continuous stream of the solution, a cooling jacket surrounding said conduit provided with liquid inlet and outlet means, said inlet means being adjustable for controlling the flow of cooling liquid into said cooling jacket, a funnel shaped crystallization chamber containing sodium sulfate crystals to an initial depth connected with said conduit at the apex of said funnel and provided with solution discharge means, a sediment level indicator positioned in said chamber for sensing any variation in the initial depth of crystals collected therein, means connected with said sediment level indicator for controlling the inlet of said cooling jacket whereby the cooling of said spin bath is continuously regulated according to the crystal depth in said chamber, and means within said chamber for measuring the temperature of the solution passing therethrough whereby the crystallization point of said solution is continuously determined.

8. A method for continuously determining the crystallization point of a circulating spinbath used in the viscose process, comprising the steps of

(a) cooling a stream of spinbath to a point where crystallization just starts to occur,

(b) passing the stream of cooled spinbath through a layer of sodium sulfate crystals of known thickness,

(c) detecting any changes in thickness of the layer of the crystals,

(d) varying the amount of cooling of the stream in response to said changes to maintain a substantially constant thickness in the layer of sodium sulfate crystals, and

(e) measuring the temperature of the spinbath at a point adjacent the layer of sodium sulfate crystals.

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LOUIS R. PRINCE, *Primary Examiner.*

JOSEPH P. STRIZAK, RICHARD C. QUEISSER, *Examiners.*