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DEHYDRATION OF CAUSTIC ALKALI

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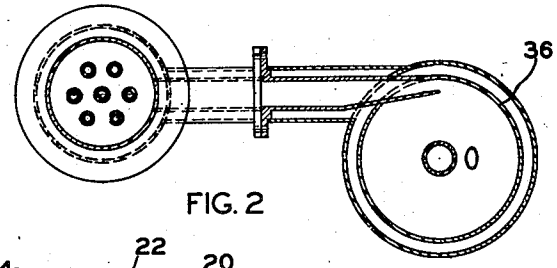
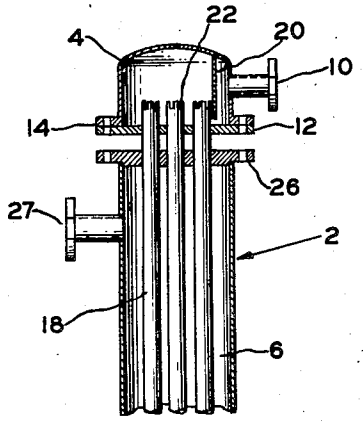


FIG. 2



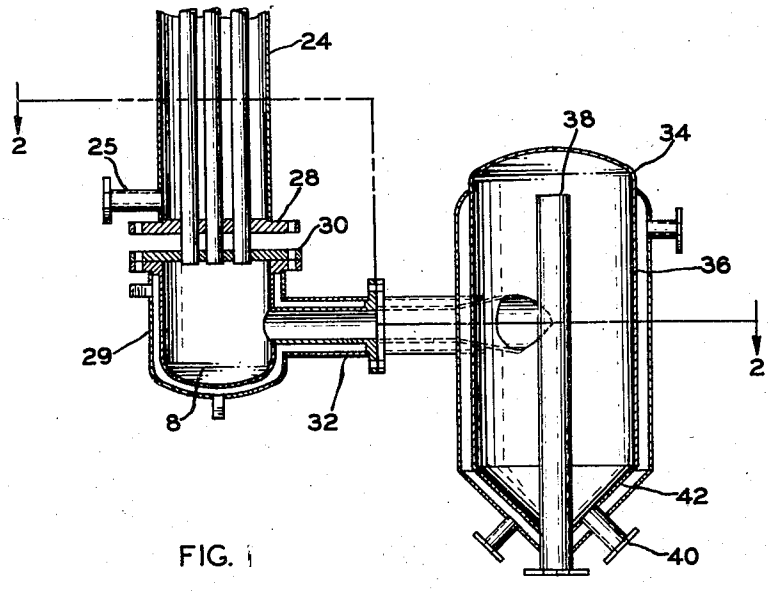


FIG. 1

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DEHYDRATION OF CAUSTIC ALKALI

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8 Claims. (Cl. 23—184)

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This invention relates to a method of dehydrating caustic soda solutions, and more particularly relates to a method of obtaining substantially anhydrous caustic soda, which method is characterized by the introduction into the caustic soda during the process of dehydration of substantially no more impurities than possessed by the original caustic soda solution.

The problem of obtaining pure anhydrous caustic soda is an old one in chemical arts. Anhydrous caustic soda is an article of commerce and is obtained at present in the anhydrous form by the use of pot stills in which caustic soda is gradually heated to temperatures of the order of 900° F. over a period of several days until all of the water is driven off. Not only is the time consumed in this prior art process highly impractical, but it has been found that the pots in which the caustic soda is concentrated last for but a short time and the rebuilding thereof has amounted to a tremendous expense. In addition, the consumption of fuel in the rendering of caustic soda anhydrous is high in view of the long periods of time in which the heating must continue at high temperatures.

Sundry means of avoiding the use of caustic soda pots have been proposed in the prior art, including general suggestions of reducing water content in vacuo, a principal disadvantage of which has been that by foaming of the caustic soda solution during the course of anhydrization, substantial operating difficulties are encountered. It has also been proposed to use an externally heated rotating inclined silver-lined tube from which oxygen is excluded and in addition, various proposals have been made for variations of pressure and temperature, depending upon the concentration of caustic soda achieved in the course of removing water therefrom. Additional proposals have been to employ anhydrous ammonia wherein the expense of obtaining and handling ammonia is quite substantial, and to dehydrate caustic soda in the presence of non-volatile oils to obtain a product having a coating on the crystals thereof. The last mentioned method of dehydrating caustic soda has, of course, the disadvantage that the non-volatile oil cannot be completely removed from the product whereby purity is impaired. Various proposals have also been made to heat caustic soda in contact with carbon surfaces, which require action entirely in the absence of air lest carbonates be formed but these proposals have also failed to solve the problem, particularly in view of the well-known structural weakness of carbon.

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It has also been proposed to prepare anhydrous caustic soda by treating the same in stills and the like at excessive temperatures of the order of 750–1000° F., in order to disassociate all of the water with the caustic soda therefrom. While these systems, subject to the limitation of corrosion of equipment, may actually produce anhydrous caustic soda, the cost of operating the same purely from the heat input standpoint alone is so substantial as to render impractical their operation, particularly in view of the economic limitation of obtaining the caustic soda at a cost less than that required to obtain the same in a pot still system.

The fact that pot stills are still in use in most of the major caustic soda manufacturing operations testifies to the absence of a solution of the elimination of pot stills by the various other prior art proposed methods.

The present invention envisions in general the preheating of a concentrated solution of caustic soda to bring the same to a temperature approaching its boiling point, followed by the passing of the solution downwardly against a surface maintained at a temperature in excess of the melting point of anhydrous caustic soda, to form a two-phase system of anhydrous caustic soda and superheated water vapor, the operation being preferably performed under less than atmospheric pressure. This two-phase system, while maintaining the vacuum and temperature, is passed to a separating zone wherein the mixture is impinged at a high velocity against a wall, the temperature of which is maintained above the temperature of melting of anhydrous caustic soda, provision being made in the separating zone for removal of the superheated water vapor and liquid anhydrous caustic soda at spaced points therein. The invention is also characterized by the employment throughout the zone in which temperatures in excess of the melting point of anhydrous caustic soda are employed of completely inert materials, whereby no additional impurities are added to the feed of caustic soda solution which is being treated.

The removal of substantially all of the water associated with caustic soda presents peculiar problems of handling, arising from the tendency of the material at certain temperatures and pressures to form solid phases, from the highly corrosive character of the material, and from the apparent tendency of highly concentrated caustic solutions to superheat.

It is known, for example, that there is a solid hydrate of caustic soda which forms in the tem-

perature range of 480° to 560° F., when the vacuum on a system comprising an aqueous caustic solution rises much above 16 inches of mercury, and where the caustic concentration is of the order of 90% to 95% NaOH. As the method of the present invention precludes handling of any solid phase until the treatment of the caustic is complete, it is preferred to avoid this solid phase by avoiding a vacuum much in excess of 16 inches, at most 20 inches, in the critical range of caustic concentration given above and also to bring the caustic to a temperature above its anhydrous melting point, i. e. 620° F., as quickly as possible and to maintain it at above that temperature throughout the subsequent treatment. By so maintaining the temperature, difficulties from freeze-ups of caustic approaching anhydrous condition either in the lower part of the evaporator or subsequently in the separator are obviated.

Moreover, a feature of the present invention is the discovery that a falling film of caustic solution, when moving at relatively high velocity and against a surface maintained at a temperature in excess of the melting point of anhydrous caustic, either does not pass through this solid hydrate phase, or passes through it so quickly that sufficient crystal formation, to result in the presence in the evaporator tubes of an appreciable solid phase, does not occur. The precise phenomena involved are not clearly understood but it has been found that under the described conditions and even with a vacuum as high as 20 inches, no difficulties are encountered of solid phase formation. In part this may be accounted for by the fact that increasing velocity of the highly superheated water vapor, as it travels downwardly through the tubes, reaches a point where liquid finely divided increasingly water-free caustic is removed from the walls of the tubes and entrained in the vapors, thus assuming substantially the velocity thereof. This effect is so pronounced that at or near the bottom of the tubes, no falling film remains upon the walls of the tubes, the entire content thereof comprising a mixture of water vapor and more or less water-free caustic being in the state of a combined vapor and suspension moving downwardly at very substantial velocity. Moreover, the fact that superheating of highly concentrated caustic solutions has been observed may contribute in part to an explanation of this phenomenon. In any event, where the caustic solution enters the evaporator tubes at downward velocity zero and increases in velocity under the conditions of temperature and pressure, which have been described herein, until a velocity of the order of 100 feet per second of the two phases extent in the tubes is achieved at the entrance to the separator, impingement of the phases of water vapor and caustic in liquid or vapor-suspended form at these velocities effects the removal of traces of water from the caustic heretofore believed removable only by prolonged high temperature treatment.

Inasmuch as the treatment of caustic by the method of this invention occupies but a fraction of a minute for a given sample of solution, from solution to substantial anhydrous product, and further since the apparatus in which the invention may be practiced is relatively inexpensive, considering the highly desirable results obtained and considering particularly the substantial reduction in maintenance cost, a large unit of apparatus can be economical but even a very small unit has substantial capacity due particularly to the absolutely continuous character of the operation.

An important aspect of the present invention is the production of anhydrous caustic soda without employing temperatures greatly in excess of the melting point of anhydrous caustic soda. Thus, it has been found that the method of the present invention may be operated at temperatures of the order of 50° to 100° F. above the melting point of anhydrous caustic soda (620° F.), such as 690° F., and caustic soda having a water content of less than ½% consistently obtained. It will be appreciated that this is in contrast to sundry prior art proposals, where temperatures of the order of 1000° F. are necessary to obtain the same product. The saving in expense involved in this lower temperature operation will be apparent to those skilled in the art.

In the accompanying drawing is shown a preferred form of apparatus in which the method of the present invention may be practiced, it being distinctly understood that the method is by no means limited to the particular apparatus shown but that the apparatus is merely set forth as a form which has been found to produce caustic soda having less than ½% of water combined therewith. In the drawing,

Fig. 1 is a vertical sectional view of a combined evaporator and separator in which the method of the present invention may be practiced, and

Fig. 2 is a horizontal section taken on the line 2—2 of Fig. 1.

Referring to the drawing, the evaporator, shown generally at **2**, comprises header **4**, evaporator chamber **6**, and receiver **8**. The header **4** is provided with an inlet **10** for caustic solution to be treated, the solution being derived from any convenient source and, as will be pointed out hereinafter, preferably having been preheated to a temperature approaching its boiling point. The feed solution is held on tube sheet **12**, which preferably is joined by a liquid-tight joint to header **4** by flange **14**, as shown. Evaporator tubes **18** preferably extend to a distance through sheet **12** into the space confined by header **4**, which insures that the caustic level is maintained above the lowermost extent of baffle **20**. Tubes **18** are preferably provided with wier slots **22**, whereby the amount of caustic solution which flows down the inside of the tubes may suitably be regulated to insure even feed to all of the tubes.

Side wall **24**, tube sheet **26**, and lower tube sheet **28** define a closed zone not in contact with the interior of tubes **18**, through which is flowed through passages **25** and **27** any suitable heat transfer medium which may be liquid, condensing vapor, gaseous, or the like and is especially suitably of such physical character that the vapors thereof condense on the outer walls of tubes **18** at the working temperature of the apparatus. Particularly desirable in this connection has been found diphenyl or diphenyl oxide and of particularly desirable use in this connection is a eutectic mixture of 26.5% of diphenyl and 73.5% of diphenyl oxide, which mixture has a melting point of 53.6° F. and a normal boiling point of 500° F. Since the temperature to be maintained on the inside surface of tubes **18** must be preferably in excess of the melting temperature of anhydrous caustic soda, it will be appreciated that the above mixture of diphenyl oxide and diphenyl will be employed in the cham-

ber 6 in vapor form and will exert its heating influence on tubes 18 by condensing on the outside walls thereof. The heat exchange fluid may be circulated at the desired temperature by any suitable boiler or the like not shown, the entrance and exit of the heat exchange medium being shown at 25, 27.

Tubes 18 lead through tube sheet 30 into receiver 8 which is suitably jacketed as at 29, the space between the interior of the receiver 8 and the jacket 29 also being supplied with heat exchange material at a temperature in excess of the melting temperature of anhydrous caustic soda. Connecting tube 32, leading from receiver 8 to separator 34, is also jacketed for the receipt of heat exchange material on the outer periphery thereof. The connector 32 preferably enters the separator 34 tangentially in order to impinge the vapors passing therethrough against the curved surface of inner wall 36 of the separator 34. The separator is provided with a vapor outlet 38, which extends from the bottom of separator 34 to a point near the top thereof, and with caustic soda outlet 40 mounted in the cone-shaped bottom 42 of the separator 34. The separator 34 is provided with a jacket in which heat exchange medium may suitably be circulated for maintaining the interior surface of the separator 34 at a temperature in excess of the melting temperature of anhydrous caustic soda.

As is well-known, caustic soda, in high concentration in aqueous solution and to some extent in its anhydrous form, is highly corrosive and hence easily picks up various metallic impurities. It is therefore preferable that caustic soda solution to be treated by the method of this invention be of a relatively high purity with respect to foreign ions before it is introduced into the dehydration system. Moreover, it is preferred that those parts of the dehydration system, which come in contact with caustic soda, particularly in concentrations of the order of 85% and above, and particularly at the temperatures at which these concentrations are contacted with parts of the apparatus, such as the melting temperature of anhydrous caustic soda, be fashioned of metals which are entirely inert to caustic soda in such conditions. It has previously been suggested to use nickel for such purposes but it has been found, in accordance with the present invention, that it is preferable to employ silver surfaces for contact with caustic soda in this condition. Accordingly, it is the preference of this invention to line the tubes 18, particularly at the zone of greatest evaporation, i. e. the upper portion of the chamber 6, with silver liners (not shown) and similarly to line the receiver 8, the connector 32, and the separator 34, particularly in the zones immediately above and below the zone of entrance of the mixture of caustic soda and water vapor, which enters through the connector 32.

The method may be practiced in accordance with the teaching of the present invention as follows: Caustic soda aqueous solution, of the order of 50% or more in concentration and preheated to slightly below its boiling point, is introduced into the header 4 through the inlet 10 and builds up a liquid level on top sheet 12 and behind baffle 20 until the height of the wier slots 22 is reached, whereupon the caustic soda solution trickles down the inside walls of the tubes in a thin film. The tubes having previously been raised to a temperature in excess of the melting temperature of anhydrous caustic soda, the water

combined with the caustic soda is immediately vaporized therefrom and in view of the great increase in volume of the constituents being treated, travels downwardly through the tubes 18 at a greatly increased velocity as the lower zones of the tubes are reached. At or near the bottom of the tubes, the molten nearly water-free caustic leaves the walls of the tubes presumably under the influence of the frictional effect of the high velocity water vapor, though no limitation is to be implied from this explanation as the phenomenon is not completely understood and the explanation is merely the best presently available. The system in the lower portion of the evaporator tubes comprises substantially anhydrous caustic soda in the form of a fog or mist of solid or melted particles entrained in greatly superheated water vapor. This mixture issues from the bottom of the tubes 18 into the receiver 8. Inasmuch as the receiver 8 is maintained at the same temperature as the tubes by means of heat transfer fluid circulated in the chamber defined by the outside wall of receiver 8 and jacket 29, the mixture of substantially anhydrous caustic soda and water vapor passes at high velocity through the connector 32 and into the separator 34, entering, as is shown particularly in Fig. 2, on a tangential angle into the separator 34, whereby the mixture is impinged at great velocity against the surface 36 which, as in the other portions of the apparatus, is maintained at a temperature in excess of the melting temperature of anhydrous caustic soda. The impingement of this mixture against the wall at high velocity and the spreading of the caustic soda by force in a very thin film on the wall 36 deprives the caustic soda of the small residue of water combined therewith and further sets up a centrifugal circulation in separator 34, whereby the water vapor moves towards the middle of the separator and to the vapor outlet 38, and the liquid anhydrous caustic runs down the walls of the separator to the caustic soda outlet 40, which is preferably maintained in view of the vacuum on the system by any convenient means well above the level of liquid caustic soda being collected in any suitable collector, not shown.

The method of this invention may be practiced in various and sundry other apparatus, it having been found preferable to operate in a falling film type of evaporator employing evaporator tubes which are surrounded with a suitable heat transfer fluid, wherein the temperature of the walls of the tubes are maintained in excess of the melting temperature of caustic soda. Thus, it is possible to operate by trickling the caustic soda solution down an inert metallic sheet and maintaining the sheet under reduced pressure, as well as maintaining the temperature of the sheet in excess of the temperature at which anhydrous caustic soda melts. The materials can be collected from this sheet by any suitable enclosed vessel and sent to a separator, either that shown in Figs. 1 and 2, or any other suitable separator, as will be understood by those skilled in the art.

Despite its ability to work in other apparatus, the method of the present invention has been extensively tested in the apparatus illustrated in the present disclosure and has been found to produce caustic soda of a water content of less than 1% and usually less than 0.5% over long periods of operation.

The present method is peculiarly adapted for operation on a continuous basis and has the particular advantage that once the apparatus is

set up and running, little if any attention thereto is necessary, whereby considerable savings in the manufacture of caustic soda are effected by reduction of labor necessary to service the evaporation method. The method of the present invention moreover is suitable for application in the anhydrization of lime soda caustic soda, or electrolytic caustic soda, as the supplies available for dehydration may appear.

It has been found that the presence of oxygen tends to darken the color of the caustic soda, which preferably is pure white as received from separator 34; it is therefore preferable to operate the present system in the entire absence of air or oxygen. It will be appreciated that upon placing a suitable vacuum on the system, the production of a large amount of water vapor, particularly in the tubes 18, will almost automatically prevent the presence of oxygen or air in the system.

A particular advantage of the present method lies in the absence of necessity of pumping concentrated caustic solutions and particularly of recirculation of such solutions. One of the principal disabilities of prior art proposals for doing away with the ancient caustic dehydration pots has been the necessity of recycling concentrated caustic solutions, particularly at high temperatures at which the caustic solutions are especially corrosive. These prior art proposals have in the main failed because of the necessity of having pumps in the system, since the corrosive character of the caustic soda solutions is such that pumps to recirculate such solutions did not have sufficient life in service to justify practicing of such method. It will be observed upon examining the method of the present invention, either as practiced in the particular apparatus of Figs. 1 and 2 or when practiced in other apparatus, that no pumping of caustic soda solution, whether in its concentrated or in its anhydrous form, is necessary, the force of gravity and the maintenance of suitable vacuum on the system being sufficient not only to cause the liquid to descend through the tubes 18 but also to insure that sufficient velocity is present from the receiver 8 to the separator 34, so that sufficient force of impingement of the combination of water vapor and substantially anhydrous caustic against the inner walls 36 of separator 34 will result in the separation of minor traces of water remaining in the caustic soda after passage through the evaporator, whereby the caustic is collected in substantially anhydrous form.

With respect to the apparatus of Figs. 1 and 2, which has been found particularly useful in the practice of the present invention, attention is directed to the tube sheets 12 and 13, which it will be observed are out of contact with each other. This double tube sheet arrangement has been found to work satisfactorily since it prevents the boiling of the caustic solution on the top of tube sheet 12 or at least substantially eliminates that boiling, whereby uneven feed to the tubes 18 through the wier slots 22 is also avoided. In the course of practicing the present method in the apparatus as shown in the drawing, it has been found desirable to have as even feed as possible to each of the tubes in the tube bundle, whereby no single tube is over-loaded and no single tube fails to operate at full capacity. The over-loading of a tube has been found to produce a substantial amount of water in the final product as recovered from the outlet 40 of the separator 34, and the underloading of a tube, of course, may be expected to reduce the capacity of the entire unit.

The method of the present invention may be applied to feed solutions of any desired initial concentration but is particularly adapted for the treatment of caustic soda solutions having concentrations of the order of 50% or more, such as 50% caustic soda, which is a well-known article of commerce, or 70% caustic soda, which is similarly well-known. Moreover, although the method is particularly described in connection with the treatment of sodium hydroxide, it may be used in connection with the rendering anhydrous of other alkali metal hydroxides, particularly potassium hydroxide.

While there have been described in detail certain forms of the invention and embodiments of its practice, the invention is not to be understood as being limited to the detailed disclosure as it is realized that changes within the scope of the invention are possible, and it is further intended that each step in the following claims shall refer to all equivalent steps for accomplishing the same result in substantially the same or equivalent manner, it being intended to cover this invention broadly in whatever form its principle may be utilized.

What is claimed is:

1. The method of dehydrating caustic alkali to a water content of less than 1%, which includes the steps of passing an aqueous solution of caustic alkali downwardly by gravity in a thin film on a surface maintained at a temperature in excess of the melting point of anhydrous caustic alkali and under less than atmospheric pressure, to form a mixture of superheated water vapor and anhydrous caustic alkali, and effecting the separation of the components of said mixture at a temperature in excess of the melting point of anhydrous caustic alkali, said dehydrated caustic alkali being obtained in a single pass down said surface.

2. The method of dehydrating caustic soda to a water content of less than 1%, which includes the steps of passing an aqueous caustic soda solution downwardly in a thin film on a vertical surface maintained at a temperature in excess of the melting point of anhydrous caustic and under vacuum, to evaporate in a single pass substantially all of the water associated with the caustic, forming a two-phase mixture of caustic and water vapor, impinging said mixture at high velocity upon a surface maintained at a temperature in excess of the melting point of anhydrous caustic, while maintaining said vacuum, and separately recovering said caustic and said vaporized water.

3. The method of dehydrating caustic soda to a water content of less than 1%, which includes the steps of preheating a caustic solution to a temperature slightly below its boiling point, passing the so-preheated solution downwardly by gravity in a thin film against a surface maintained in a vacuum not greater than 20 inches of mercury and at a temperature in excess of the melting point of anhydrous caustic, to obtain in a single pass a mixture of anhydrous caustic and superheated steam, impinging said mixture at high velocity against a surface having a temperature in excess of the melting point of anhydrous caustic, and separately collecting said steam and said caustic soda.

4. The method of dehydrating caustic alkali to a water content of less than 1%, which includes the steps of passing an aqueous solution

of caustic downwardly by gravity in a thin film on a surface maintained at a temperature less than 100° F. above the melting point of anhydrous caustic and under less than atmospheric pressure, to form in a single pass a mixture of superheated water vapor and finely dispersed caustic, and effecting the separation of the components of said mixture at a temperature in excess of the melting point of anhydrous caustic.

5. The method of dehydrating caustic alkali to a water content of less than 1%, which includes the steps of passing an aqueous solution of caustic downwardly in a thin film on a vertical surface maintained at a temperature at less than 100° F. above the melting point of anhydrous caustic and under a vacuum of less than 20 inches of mercury, to form in a single pass a mixture of superheated water vapor and entrained caustic, and effecting the separation of the components of said mixture at a temperature in excess of the melting point of anhydrous caustic.

6. The method of dehydrating caustic soda to a water content of less than 1%, which includes the steps of passing caustic soda solution having a concentration of at least 50% in sodium hydroxide downwardly by gravity in contact with an inert surface, while maintaining said surface at a temperature in excess of the melting temperature of anhydrous caustic soda, to evaporate in a single pass a substantial portion of the water of said caustic solution in vapor form and superheat the same, and impinging said caustic and said superheated vapor tangentially at high velocity against an inert curved surface to set up a centrifugal effect whereby said caustic, substantially freed of its water vapor, is collected on said surface and said water vapor leaves said surface, said separation being accomplished while maintaining said surface at a temperature in excess of the melting temperature of caustic soda.

7. The method of dehydrating caustic alkali to a water content of less than 1%, which includes the steps of once passing an aqueous solution of caustic downwardly by gravity in a thin film on a surface maintained at a temperature at less than 100° F. above the melting point of anhydrous caustic and under a vacuum of less than 20 inches of mercury, evaporating water in the form of highly superheated vapor from said surface and simultaneously increasing the velocity of said vapor moving against said surface, entraining caustic alkali from said film in said vapor, and separately collecting water vapor and caustic alkali having less than 1% of water associated therewith.

8. The method as claimed in claim 7 in which said vapor and said caustic alkali are separated by impinging said mixture tangentially against a curved surface maintained at a temperature in excess of the melting point of anhydrous caustic alkali.

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