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Ludwigshafen. Patent Division

To: Dr. Herold
Dr. Brude

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New Application: "Process for the Separation of
Alcohols from Non-Aqueous Liquids"

Enclosed we are sending you an outline, with sketch, of a new Patent application concerning a process for the isolation of alcohols which has given very good results at our plant. It is based on the known esterification method by means of boric acid, which we have developed into a technical process of easy and good operation. We assume that the Patent ownership of Schimmel & Co. (Germ. Patents 406 768, 444 640, 448 419) and the recently published application of Ludwigshafen (O.Z. 12 108) are known.

In view of the pending projects (Auschwitz), which will soon require a conference with outside firms, we respectfully request that this application be studied and sent in as soon as possible.

AMMONIA WORKS MERSEBURG

Enclosures.

PROCESS FOR THE SEPARATION OF ALCOHOLS FROM NON-AQUEOUS LIQUIDS

It is known that alcohols, upon addition of boric acid and gentle heating, are easily converted into the corresponding boric acid esters; thus, compounds of substantially higher boiling points are obtained. It is furthermore known that, under the influence of water, these esters may be easily split, so that alcohols are obtained in pure form. If the desired alcohol is in mixture with other substances, such as hydrocarbons and others, which have the same boiling point as the alcohols, one converts the latter into the high boiling ester and removes the undesirable components by distillation. Then, after saponification, the alcohol is obtained in pure form.

Now, it was found that in this process relatively high boric acid losses occur when the boric acid solutions are evaporated during the saponification of the esters and the washing out of the alcohols; this procedure is used in order to regain the boric acid in solid form. Furthermore, the evaporation of such large amounts of water requires considerable energy and corresponding equipment which cannot be built from ordinary materials

There is, furthermore, always a certain definite loss connected with the separation of the saponification water from the alcohol; the loss is caused by solution or emulsion, and it depends on the molecular weight and structure of the particular alcohol. The recovery of these alcohol portions is often not worth while, and this entails a consequent loss in yield.

It has now been discovered that the disadvantages listed

above may be eliminated to a great extent, provided the saponification (sic) of the boric acid ester is carried out at higher temperature with an aqueous boric acid solution; and that the latter is separated from the alcohols at the same, or slightly lower temperature, preferably by sedimentation; the boric acid solution is then cooled outside the saponification vessel, and the boric acid which precipitates is separated by filtration; the filtrate is then recycled into the saponification vessel, while the solid boric acid is again led into a new mixture from which alcohol is to be separated.

It was discovered, surprisingly enough, that the saponification is possible not only with pure water, but also with aqueous boric acid solutions which, according to this newly-invented process, are led in cycle. One should, at this point, take into consideration the fact that the boric acid solution freshly added to the alcohol is relatively dilute, i.e. saturated at normal or less than normal temperature; but that, due to the free boric acid formed during the saponification process, this solution is continually enriched so that at the end, at high temperatures (such as e.g. 98°), one arrives at a practically completely saturated solution. It is especially surprising to find that, despite this increase of the boric acid concentration, the saponification in favor of the free alcohols requires only relatively small amounts of boric acid solution; thus, aqueous boric acid solutions of concentrations varying between 90% and 100% of the degree of saturation, can form at the saponification temperature (e.g. 95-98°).

Another surprising phenomenon was observed: the portions of boric acid still left in the alcohols after saponification with the boric acid solution are relatively small, so that the amount of wash water needed for their removal is insignificant. It will be most practical to measure the boric acid solution for the saponification in such a manner that the solution, after completion of the saponification of the ester, will have a boric acid concentration from 35-60% of the saturation value at the saponification or sedimentation temperature. With this kind of procedure, much boric acid will still separate from the solution upon cooling.

Furthermore one gets the advantage of having only very small amounts of boric acid in the alcohol layer, and this in turn makes it possible to use relatively small amounts of water for the required rinsing.

For the preparation of pure alcohols according to the described method, all the known types of alcohol can be used. By this method one may obtain aliphatic, aromatic or alicyclic alcohols, or alcohols consisting of a mixture of these types. The aromatic types may be substituted or condensed in any form whatever, e.g. they may be condensed into multiple ring aromatics, and at the same time the alcohol group may be either in one of the nuclei or attached to a side-chain. The alcohols may also have one or more hydroxyl groups. However, it will be most practicable to use the process only for those alcohols which are distillable, since it is only with this type of alcohol that an exceptionable advantage may be obtained from the esterification

with boric acid, and with it a conversion into higher boiling products. With non-distillable alcohols this advantage is lacking. Such types of alcohols are, for instance, sugars and similar substances. The process described is furthermore not the best suited method for the lower members of the aliphatic straight chain alcohols, but it is well suited for those alcohols which are insoluble, or only sparingly soluble, in water, such as for instance butyl alcohol and its higher homologues.

The process is of special value for the separation of the alcohols which are obtained by the reduction of carbon monoxide with hydrogen under pressure, mainly with the use of iron-containing catalysts. In this case, the undesirable by-products from which the alcohols must be separated are mainly saturated and unsaturated hydrocarbons. In this synthesis, products ranging from the lowest to the highest chain lengths are known to form. Those components from which the alcohols are to be separated, should be broken down into distillation cuts in such a way that the alcohols, which after esterification are converted into high boiling esters, will have a considerable boiling distance from them.

The esterification of the alcohol-containing mixtures is best carried out at elevated temperature. For best results, this temperature should be chosen so that the removal of the esterification water will be possible by a simple method. The water can simply be distilled off or an auxiliary liquid (after Pat. Appl. J. 99 923 IVc/12 o = O.Z. 12 108) can be used for the carrying off of the water, e.g. benzene, toluene, etc.

The esterification is carried out with solid boric acid. It may be used in slightly moist condition, i.e. in the form in which it is obtained in the cyclic process according to the present invention. The esterification may be accelerated and uniform distribution of the boric acid insured by stirring or by other devices.

The esterification may take place in the same container in which later the distillative removal of the by-products - e.g. the hydrocarbons - will be effected. After these by-products have been removed, the newly invented process calls for saponification of the boric acid esters by bringing them into close contact with an aqueous boric acid solution. The operation is to be carried out so that at the end of the reaction the temperature is close to the boiling point of water, e.g. at normal pressure, 95-98° or less. In many cases it will be of advantage if the pressure is increased. The saponification can then be carried out at somewhat higher temperature, which means that the reaction rate is increased and at the same time the solubility of the boric acid in water is also enhanced. The best method for achieving intimate and thorough mixing of the aqueous solution and the organic components, is intensive stirring. This may be done by mechanically operated stirrers, by passing through of gases or vapors (such as steam and others), by repumping of the liquids, e.g. by means of centrifugal pumps, etc., etc.

After completion of the saponification one should, in order to insure a clean-cut separation between the alcoholic and the aqueous layer, leave the saponification vessel alone for a

while and remove whatever boric acid solution accumulates at the bottom. It will be well to keep this step in mind when designing the shape of the saponification vessel: the walls, floors, stirring gears etc. should all be such that the separation of the two layers can be made as quantitative as possible. The saponification vessel should be maintained at as constant a temperature as possible during the period in which the layers separate, by maintaining this constant temperature, thermo-currents or precipitation of boric acid by cooling of the aqueous solutions, are to be prevented. Furthermore, it will be preferable in many cases to shut out the oxygen of the air during the period of saponification in order to prevent undesirable oxidation reactions.

When the hot, partly or entirely saturated, boric acid solution is cooled, the boric acid separates in solid form. One may cool the solution as much as one wants, for instance down to 20° by using ordinary cooling water, or one can approach very closely the possible limit of 0°, say +2°. The solid boric acid is separated from the mother solution by the usual known methods, e.g. by filtration through suction funnels, filter presses etc. Other separation methods too may be used, such as decantation, centrifugation, etc.

It is important that the boric acid be obtained in easily filtrable form. This can be insured by regulating the rate of cooling, the behavior of currents, etc. The cooler, the pipes, etc. will be such that the deposition of boric acid will not occur on undesirable spots, and if it does occur, the boric acid must be easily removable.

The boric acid now recovered is led back into the cycle and added to a fresh batch in which the alcohol is to be esterified. The boric acid can be used in slightly moist condition, i.e. in the form in which one obtains it after centrifuging. However, one can also free it from these small amounts of water, either by displacement of the water with organic liquids or by passing over of dry gases; in certain cases this may be done at higher temperature, by heating the boric acid, etc.

The mother solution is led back for saponification of further batches of ester.

The alcohols obtained after saponification and after separation from the aqueous solutions still contain small amounts of boric acid. These remnants of boric acid can be best removed by washing with water. Again, this washing process should be carried out at higher temperature, especially when high molecular alcohols are involved, since they are then less viscous. It is furthermore recommended that the washing be carried out by the known countercurrent method. One can thereby operate discontinuously along the following lines:

The washing process is divided into several individual stages, say three or more; for the last, high-purification, stage one uses fresh water free from boric acid whereas the enriched boric acid solution obtained in each stage is led back into the previous stage. From the last stage, which contains the concentrated washing solution, enough boric acid solution is transferred to the saponification cycle as corresponds to the disappearance of water for the saponification reaction. From the residual

concentrated washing solution, the boric acid is isolated and recovered by evaporation. After this purification process, the alcohols can in most cases be directly utilized without further processing.

The process can be operated in all stages both continuously or intermittently. Between the individual stages, storage vessels may be inserted which allow a certain buffer effect between the various operating stages.

Example 1

In a synthesis of organic compounds, carried out with carbon monoxide and hydrogen under a pressure of 20 atm. and in the presence of an iron catalyst, a product of the following composition was obtained:

50% alcohols
40% olefins
9% paraffin hydrocarbons
1% acids, ketones, etc.

When divided into boiling fractions, the following components were obtained:

0-100°	30%
100-200	20%
200-300	16%
300-400	17%
Residue	17%

In order to obtain the alcohols contained in the components from 200-400°, the two fractions were treated as follows after having been separated:

For example, 100 kg of the fraction 300-400° - corresponding to an alcohol concentration of 72% by weight - are heated to 90°C. in the esterification container A, together with 6.6 kg

boric acid and 575 kg benzene as auxiliary esterification liquid. The mixture is strongly stirred. In the course of two hours, 575 kg of benzene and 4.8 kg of water distill. The vapors are condensed in a cooler B and the liquids separated from each other in a separation container C; from this container the benzene can also be led back for further use. Subsequently, the distillation will be continued in vacuo. Thus, the hydrocarbons present in the original boiling component are driven off, condensed in cooler B and collected in a separator D, from where they can then be let out (28 kg). The boric acid ester mixture which remains in the esterification still A is now passed, in liquid phase, into the saponification container E where it is saponified together with 55.5 kg of a 2.6% aqueous boric acid solution at 95° under intensive stirring for one half hour. Following this, stirring is stopped and the temperature is maintained at 95°; this will allow the layer separation between the boric acid solution and the newly formed alcohol mixture, to take place; about half an hour of standing is required. The hot boric acid solution, which by now contains 10.9% by weight (= 38.8% of the saturation value at 95°) boric acid is drawn off through the three-way stopcock G, passes sightglass F, and goes into condenser H; the sightglass F allows the layers to be easily distinguished.

In condenser H, thorough cooling of the boric acid solution down to +2° takes place, and the boric acid separates in crystalline form. At the same time, a stirrer I moves inside the container. In condenser H, the boric acid deposits on the bottom of the container and is led into a continuously operating centri-

fuge K; from here, it is removed by peeling (Abschälen) and led into a storage container L. The boric acid obtained amounts to 5.2 kg. The boric acid is brought into esterification container A and used for the next operation.

The mother solution coming out from the centrifuge K is brought to a surge drum M. It amounts to 50.5 kg. From this container it can then be brought out and used for the next operation; this can be done by leading it through a pump into saponification container E.

The free alcohols formed during the saponification are also drawn off, through the three-way stopcock G, into the heated storage container O. They amount to 72 kg and still contain 1.5 kg boric acid in solution. In order to remove this boric acid, the alcohol mixture is passed, from the intermediate container O, into a washer P. Here, it is washed with 56.2 kg washing fluid. In this container P, the two layers will again be separated from each other after a suitable period of standing. The water migrates into intermediate vessel Q, whereas the alcohol runs into the next washing vessel R where it is again washed with water, to be subjected to a final water wash in container S. Here, pure water is used. The used water is led back into the pre-final washing stage R through the storage container T. From there (i.e. from R, Transl.), the now enriched water is passed through storage container U and into washing stage P. From the intermediate container Q for highly enriched wash water, it will be partly brought into the saponification cycle, between G and H.

Patent Claims

1.) Process for the separation of alcohols which are insoluble or only sparingly soluble, and distillable, from non-aqueous liquids such as hydrocarbons and other organic compounds which cannot be esterified; by fixing (the alcohols, Transl.) as boric acid esters, distilling off the remaining non-esterified mixture components, splitting of the boric acid esters with water, and separation of the alcohols. The process is characterized by the following set of procedures:

The saponification of the boric acid ester is carried out at higher temperature with an aqueous boric acid solution; the latter is then separated from the alcohols at the same, or slightly lower, temperature, preferably by letting the mixture stand; the boric acid solution is cooled outside the saponification vessel and the boric acid which precipitates is separated; the filtrate is passed back into the cycle and into the saponification vessel and the solid boric acid is brought back to a new mixture from which alcohols are to be separated by esterification.

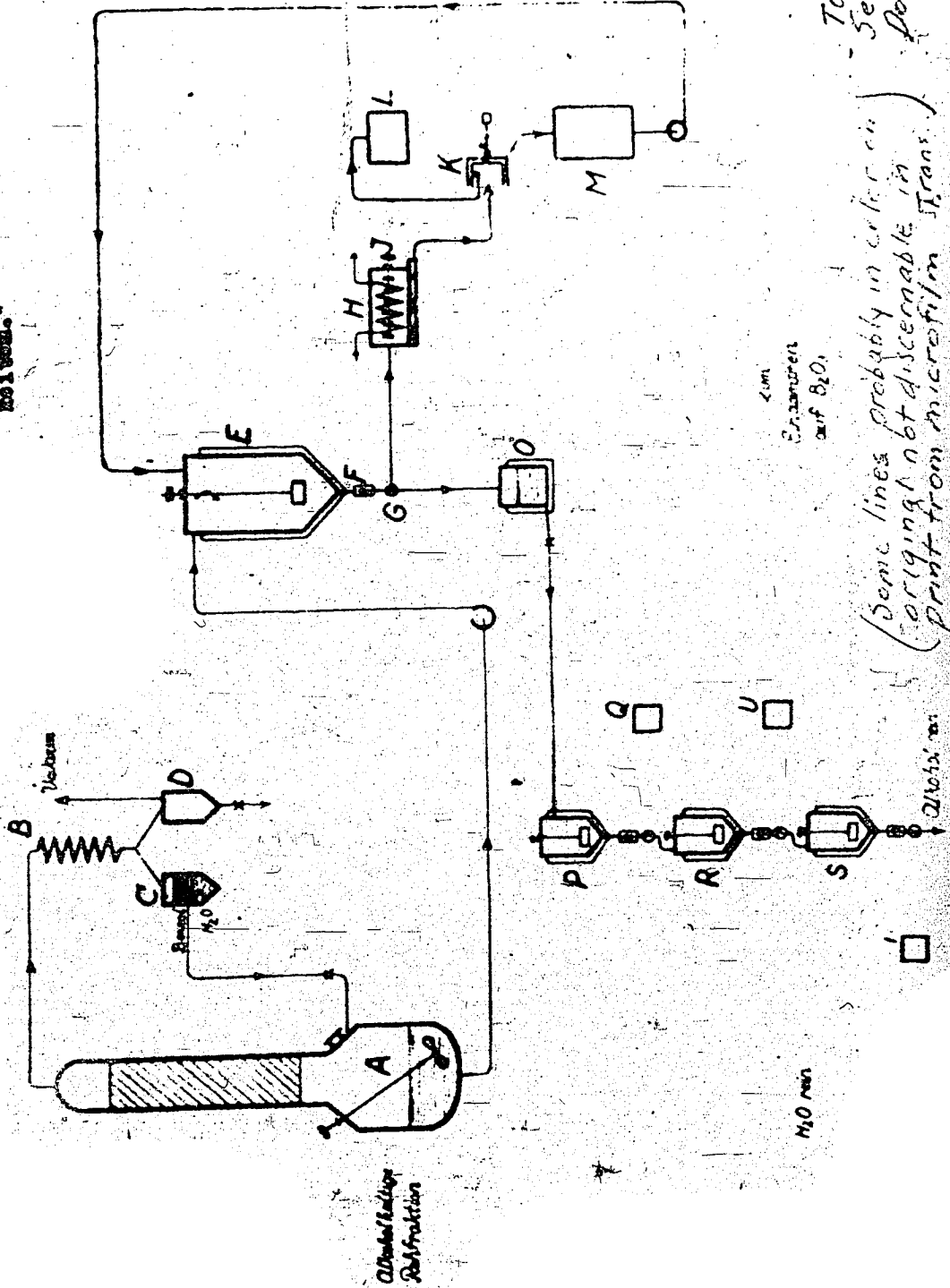
2.) Process according to Claim 1, characterized by the fact that the amount of boric acid used for the saponification is measured so that, after completion of the saponification of the ester at the esterification or standing temperature, the boric acid concentration will be 35-60%, corresponding to complete saturation at the particular temperature.

3.) Process according to Claims 1 and 2, characterized by the fact that the alcohol layer separated from the boric acid

solution after saponification, is washed, either continuously or discontinuously, with water in countercurrent; from the wash water which contains the most boric acid, enough is led back into the saponification cycle to correspond to the amount of water required for the saponification reaction; from the remaining wash water, the boric acid is isolated, advantageously by evaporation of the solution.

7. April 1941.

Im Versuchsaufbau: Verfahren zur Abtrennung von Alkoholen aus nichtferrolegierten Stählen.



Alkoholelektrolyt
Reaktion

Erwärmt
auf 820°

110 mm

Tom Neel, Ph.D.
Section II
Document 22

(Some lines probably in error in original not discernable in print from microfilm trans.)