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PROCESS OF REFINING ACRYLONITRILE BY DISTILLATION

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The invention relates to a process of refining acrylonitrile, especially the acrylonitrile made from acetylene.

Acrylonitrile has acquired considerable technical importance because of the increased use of acrylonitrile fibres, i. e. Orlon fibres. It is essential that the acrylonitrile used for the production of these fibres should be as pure as possible. Its content of polyenic impurities, especially of divinyl acetylene, has, therefore, to be very low and must not exceed 0.1%.

Two different methods are chiefly used to produce acrylonitrile: from ethylene cyanohydrin by separating water, and from acetylene by adding hydrocyanic acid. The only impurities occurring in acrylonitrile produced according to the first method are water and some unreacted ethylene cyanohydrin, as pure ethylene cyanohydrin can be used as raw material. It is, therefore, relatively simple to refine such a product by distillation.

Acrylonitrile produced from acetylene, on the other hand, contains a number of acetylene derivatives such as monovinyl acetylene, divinyl acetylene, its homologue ethinyl butadiene, chloroprene, cyanobutadiene, acetaldehyde, and lactonitrile, the boiling points of which range above and below the boiling point of acrylonitrile. An additional difficulty when refining acrylonitrile, boiling point 77.5° C., by distillation is the fact that, being only partly miscible with water, it forms a constant-boiling mixture of 88% acrylonitrile and 12 water which possesses a boiling point of 70.5° C. at atmospheric pressure. When condensed, the vapours of such a mixture form two phases, an acrylonitrile phase containing water which consists of 97% acrylonitrile and 3% water, and a water phase containing acrylonitrile which consists of 7% acrylonitrile and 93% water.

We have discovered that divinyl acetylene with acrylonitrile forms an azeotrope which consists of 37% divinyl acetylene and 63% acrylonitrile. It possesses a boiling point of 75.0° C. at atmospheric pressure. In the presence of water a ternary mixture is formed (because of the limited solubility of the water in both components) which possesses a boiling point of 67° C. Without taking the water into account the ternary mixture consists of 46% divinyl acetylene and 54% acrylonitrile; the water content amounts to about 10–15%.

Ethinyl butadiene, too, forms an azeotrope with acrylonitrile, the boiling point of which is 76.5° C. In the presence of water its boiling point is 70.0° C. The contents are relatively low judging by the ultra violet absorption and the reaction with silver nitrate. Because of these facts refining such an acrylonitrile by distillation is a complicated process, the difficulties of which we succeeded to overcome.

As mentioned above divinyl acetylene and acrylonitrile form in a dry system an azeotrope, the boiling point of which is only 2.5° C. lower than that of the acrylonitrile, 77.5° C. In the presence of water, on the other hand, divinyl acetylene and acrylonitrile form a ternary azeotrope which boils at 67° C., that is only 3.5° C. lower

than the constant-boiling acrylonitrile-water mixture. These differences of the boiling temperatures are too inconsiderable to be made use of in an ordinary technical distillation, and to remove the ethinyl butadiene is a still greater problem. We have discovered, however, that the difference between the boiling points of the acrylonitrile and the azeotrope with which the divinyl acetylene is removed can be increased by strict adjustment of certain factors, i. e., by taking steps to make the crude acrylonitrile contain exactly as much water as is necessary to form the ternary azeotrope acrylonitrile-divinyl acetylene-water, at least during that step of the distillation in which the divinyl acetylene is removed. The difference of the boiling temperatures of the ternary azeotrope acrylonitrile-divinyl acetylene-water and of dry acrylonitrile is then 77.5—67=10.5° C., and of ethinyl butadiene 77.5—70.0=7.5° C. The critical height of the water content amounts to 20 to 30% of the divinyl acetylene content. If the acrylonitrile is drier during the distillation the water does not suffice to form the ternary azeotrope with all the divinyl acetylene. If the water content is higher it causes the amount of the constant-boiling mixture acrylonitrile-water to increase which, because of the inconsiderable difference of the boiling temperatures, distils over together with the ternary divinyl acetylene azeotrope and causes the content of acrylonitrile in the "divinyl acetylene fraction" to exceed the minimum of 54% (composition of the ternary azeotrope). A certain excess of water can, however, be preferable when technically distilling in a column where dry acrylonitrile (B. P. 77.5° C.) is drawn off at the bottom, and the azeotrope divinyl acetylene-acrylonitrile-water (B. P. 67.0° C.) at the top of the column, even if the acrylonitrile content of the top fraction thereby increases, as the constant-boiling mixture acrylonitrile-water, which is thus formed, helps to strip all the ternary divinyl acetylene azeotrope from the acrylonitrile. A water content of 20–300%, preferably of 50–200%, calculated on the divinyl acetylene content has, therefore, proved to be of advantage. When using these water contents the top products contain 77% and 95% acrylonitrile respectively. As the divinyl acetylene content of the crude acrylonitrile can vary between for instance 0.3 and 1%, the water content has to amount to 0.15–2%. As acrylonitrile is usually saturated with water before the distillation and contains then about 3%, it is necessary to draw off some water before or while removing the divinyl acetylene, if the water content is to be kept within the prescribed limits. If no water were drawn off, the acrylonitrile content of the "divinyl acetylene fraction" would be unnecessarily high.

As mentioned above the "divinyl acetylene fraction" contains at least 54% acrylonitrile and even more, if the water content is higher during the removal of the divinyl acetylene. This acrylonitrile can be recovered, for instance by extraction with water and redistillation of the water phase.

The invention comprises a process of distilling acrylonitrile made from acetylene and containing water and acetylene derivatives, in a distillation column, the main column, after removing the undissolved water and the higher boiling impurities such as higher acetylene polymer etc. in a preparatory column. Impurities possessing a lower boiling point than the constant-boiling acrylonitrile-water mixture, and the azeotrope acrylonitrile-divinyl acetylene-water leave the main column at the top, part of it serving as reflux. Water phase collected in the column on one or several plates or formed by condensation of a certain amount of vapour collected on one or several plates, is drawn from the column to such a degree, that the water content of the top product amounts to 20–300% of the divinyl acetylene content. Pure acrylonitrile vapours leave the column from one of the lowest plates,

while a small amount of acrylonitrile together with higher boiling impurities are drained from the still.

The above statement, how much water is to be drawn from the column, can also be expressed in another way: in the top product a certain proportion has to exist between the divinyl acetylene and the acrylonitrile, 20% water calculated on the divinyl acetylene content corresponding to about 115% acrylonitrile of the divinyl acetylene content, which the composition of the ternary azeotrope proves. The temperature at the top of the column has to be 65–70° C. In this way lower boiling impurities, divinyl acetylene, water, and acrylonitrile can be separated in one column.

The process can also be modified in such a way that vapour or condensate consisting of acrylonitrile phase which contains water, and of water phase which contains acrylonitrile, is drawn from one of the plates in the main column where water phase separates, and is fed back into the preparatory column. The vapour or condensate drawn from the column in this way can preferably amount to between 10 and 25% of the feed. Finally the water content can be adjusted by a water separator in the reflux pipe.

Before entering the main column the crude acrylonitrile can be treated in the following way: together with the water formed during the synthesis it is fed into a preparatory column, from the top cooler of which low boiling acetylene derivatives and acrylonitrile containing water are drawn, a mixture of this solution and water which has separated spontaneously serving as reflux. Water stripped of acrylonitrile, and impurities possessing a higher boiling point than the constant-boiling acrylonitrile-water mixture, especially higher acetylene polymers, lactonitrile and cyanobutadiene, are drained from the bottom of the column. The water which, solved in acrylonitrile, escapes from the top of the column amounts to less than 3% of the product.

There are other ways of treating the crude acrylonitrile before feeding it into the main column. It can, for instance, together with the water phase be led through a gas separating column where it is stripped of the lowest boiling impurities, the operation of the main column thereby being simplified. Before entering the main column the crude acrylonitrile can also be separated from the water phase which, by separate distillation or extraction, yields a constant-boiling acrylonitrile-water mixture.

The pure acrylonitrile leaving the main column can be refined once more by distillation in an after-treatment column in the presence of a corresponding amount of water, additional acrylonitrile divinyl acetylene-water azeotrope being drawn from the top of the column, and very pure acrylonitrile vapours leaving the column at the bottom.

The divinyl acetylene content of the acrylonitrile can vary between 0.3 and 1% according to working conditions, e. g. the age of the used catalyst, the temperature, and the amount of fed hydrocyanic acid. The amount of water drawn from the main column must be varied accordingly. How much water is to be drawn off depends also on the efficiency of the main column. If the separating power of the column is good the water content can be kept directly above the water content which is theoretically necessary to form the ternary divinyl acetylene azeotrope, and the acrylonitrile leaving the column at the bottom will still be pure.

If a column of inferior separating power is to yield pure acrylonitrile it is necessary to decrease the amount of water drawn from the column, and to put up with the fact that the distillate contains more acrylonitrile than is needed to form the ternary divinyl acetylene azeotrope.

Ethinyl butadiene can also be separated by using silver-, copper-, mercury-, and other metal salts which form metal complexes with ethinyl butadiene.

Example 1

Acrylonitrile containing 0.31% divinyl acetylene (determined by ultra violet absorption) was continuously distilled in a 2.5 cm. (1") glass column which was filled with 6 x 8 mm. Raschig rings. The experiment was carried out in order to determine in laboratory scale the efficiency of a relatively imperfect technical column, the water contents of the feed varying. The distance between the top of the column and the inlet was 80 cm., between the inlet and the outlet for "pure" acrylonitrile 75 cm., and between the outlet and the still 35 cm. The rate of distillation of all experiments registered in the table was 150 ml./h. (fed acrylonitrile), the reflux was 1:20. The water contents varied. The results were:

Crude acrylonitrile		Top product		"Pure" acrylonitrile		Bottom product	
Percent DVA	Per cent H_2O	Per cent DVA	ml. drawn	Per cent DVA	ml. drawn	Per cent DVA	ml. drawn
0.31	0.1	3.2	45	0.14	450	0.10	55
0.31	0.5	1.7	82	0.05	455	0.05	63
0.31	0.7	2.3	60	0.05	463	0.05	60

As can be seen from the table it is necessary, the column being inadequate, to keep the divinyl acetylene content of the top product considerably lower than corresponds to the composition of the ternary divinyl acetylene azeotrope in order to obtain pure acrylonitrile at the bottom of the column.

Example 2

Crude acrylonitrile (made from acetylene and hydrocyanic acid with Niewland catalyst) containing about 0.7% divinyl acetylene and higher acetylene polymers (determined by ultra violet absorption), and all the earlier mentioned impurities, was distilled in a preparatory column, water, higher acetylene polymers, 1-cyanobutadiene-1.3, and lactonitrile being drained at the bottom. The acrylonitrile obtained at the top of the preparatory column which contained 0.5% divinyl acetylene, was fed into the main column.

The main column, an about 8 cm. (3") copper column filled with 6–8 mm. Raschig rings, had the following dimensions: distance between top of the column and inlet 1 m., between inlet and outlet for acrylonitrile 0.6 m., and between outlet and still (the drain) 0.4 m. 15 cm. above the inlet there was a plate where water phase, condensed within the column, was collected and drawn off. It was essential to draw exactly so much water from this plate that the divinyl acetylene content of the top fraction was kept within 10–80% of the amount of the acrylonitrile (preferably within 20–40%) at a temperature of 67–68° C. The column was fed with 1.5 l. acrylonitrile per hour. In the course of this experiment an enrichment of divinyl acetylene up to 20% (of the amount of acrylonitrile) was achieved in the distillate, and the acrylonitrile obtained from the lower part of the column contained 0.15% divinyl acetylene. This acrylonitrile was redistilled in another column, 0.3% water being added, and the divinyl acetylene content of the final product was thereby reduced to 0.02%.

We claim:

1. The method of removing divinyl acetylene from a crude acrylonitrile, which comprises the steps of subjecting the crude acrylonitrile to fractional distillation, regulating the water content in the still so that the water content in the top product at least corresponds with the water content in a ternary azeotropic mixture of acrylonitrile, divinyl acetylene and water, with a boiling point of 67.5° C. distilling off said ternary azeotropic mixture and recovering the acrylonitrile substantially free from divinyl acetylene and water at the bottom of the still.

2. The method according to claim 1 characterized in

adding water to the still at least in an amount that corresponds with the formation of an azeotropic mixture of acrylonitrile, divinyl acetylene and water with all divinyl acetylene present in the crude acrylonitrile.

3. The method according to claim 2 characterized in adding water in an amount of 20–30% of the divinyl acetylene content in the crude acrylonitrile.

4. The method according to claim 1 in which impurities boiling at a lower temperature than said ternary azeotropic mixture are distilled off therewith.

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