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RECOVERY OF EXCESS ACRYLONITRILE FROM THE CYANOETHYLATION OF COTTON BY STEAM STRIPPING

Herman F. Karnes and Arnold H. Gruber, Stamford, Conn., assignors to American Cyanamid Company, New York, N. Y., a corporation of Maine

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This invention relates to an improved method of recovering acrylonitrile in mixtures from the cyanoethylation of cellulose such as cotton.

Cyanoethylated celluloses particularly cyanoethylated cotton have important advantageous properties so that the products are of increasing commercial interest. In general, the processes of cyanoethylation involve treatment of the cellulose, such as cotton, with an aqueous solution of caustic soda or similar strong alkali followed by reaction with acrylonitrile. Cotton is the most important cellulosic material for cyanoethylation and in the remainder of this specification the invention will be discussed in terms of the cyanoethylation of cotton although what is said is equally applicable to cyanoethylation mixtures from the treatment of other forms of cellulose.

A serious problem is presented by the recovery of acrylonitrile from cyanoethylation mixtures. In most processes a very large excess of acrylonitrile is used and therefore, losses of acrylonitrile in recovery procedures constitute a significant factor in the cost of the product. In the processes which have been used hitherto the aqueous mixture from the cyanoethylation reaction is removed and excess acrylonitrile and other water soluble constituents washed out from the cyanoethylated cotton. As a result a greatly increased volume of water is introduced which adds to the difficulty and cost of acrylonitrile recovery from two standpoints. In the first place mechanical handling losses are roughly proportional to the volumes handled and the greatly increased volume resulting from the wash water causes additional handling losses. A second factor is the necessity for using largely increased amounts of heat when, as is usual, the recovery involves distillation. The large heat capacity of the volumes of water used in washing add materially to this cost factor.

The present invention avoids the difficulties hitherto encountered by using steam to remove acrylonitrile entrained in the cyanoethylated cotton after draining off as much as possible of the reaction mixture. The steam distillate separates into two layers and much of the acrylonitrile can be recovered by simple decantation. The fact that it contains dissolved water presents no problem as in reusing it, the reaction medium is aqueous in any event and the small amount of water dissolved in the acrylonitrile simply constitutes a part of the reaction medium. Even the water layer which contains a small amount of acrylonitrile in solution involves no serious recovery problem because it is comparatively small and the large amounts of water which accumulate in the former processes where the cyanoethylated cotton was washed are not encountered and recovery of the acrylonitrile from the water layer is therefore from a relatively concentrated solution instead of an extremely dilute one.

Ordinarily, the use of water in the form of steam at elevated temperatures would be expected to present a problem, because one of the unavoidable losses in the cyanoethylation process is the reaction of acrylonitrile with water in the reaction medium to form oxydipropionitrile (β,β'-dicyano-diethyl ether). This reaction takes place even at the moderate temperatures which are normally used in cyanoethylation which are of the order of 50–70° C. and is, of course, more rapid at higher temperatures. According to the present invention it has been found that if the strong alkali which is present in the cyanoethylation reaction medium is neutralized there are no significant losses of acrylonitrile in the steam distillation procedure by reason of its reaction with the steam and all of the advantages of small volume, low handling losses, and economy of fuel are obtained without any drawbacks in the way of additional side reactions which would transform acrylonitrile into other products which cannot be reused.

It is an advantage of the present invention that the neutralization of the strong alkali does not constitute an added cost as it is customary to effect neutralization before draining off the reaction medium in any event. As a result there is no added chemical cost and the advantages of the present invention are not off-set by additional reagent consumption. It is also an advantage of the invention that the neutralization is not particularly critical. In general it is desirable to neutralize to neutrality or preferably slight acidity such as a pH of from 5 to 6, however, the exact pH is not critical and the lower limit is dictated by the economic considerations that lower pH's would increase acid consumption. The upper limit is not critical but in general in the absence of stabilizers it is desirable to carry out the neutralization at least to neutrality and preferably, for reliable manufacturing operations, to slight acidity. If the neutralization is effected only to the point of moderate alkalinity in the absence of stabilization agents such as ammonia and the like there is danger of other side reactions of acrylonitrile some of which are exothermic. In other words the present invention should not be operated under conditions where there is any considerable alkalinity produced by the presence of a very strong alkali such as caustic soda. Therefore, when neutralization is referred to in the specification and claims it is understood that the neutralization should be carried out to the extent that there is no significant amount of caustic alkali remaining.

The particular temperature at which the steam distillation or stripping is effected is also not critical. In general it is not necessary to use very high temperatures and ordinary process steam can be employed. Where moderately super-heated steam is cheaply available it has advantages in rendering the stripping somewhat more rapid. However, of course, steam at extremely high temperatures and super-heats should naturally be avoided as the cyanoethylated cotton itself can be destroyed by very high temperatures. In any given operation the best steam temperature to be used is dictated largely by a compromise between the cost and availability of the steam and the longer time required when a very low temperature saturated steam is used. The fact that the temperature is not crtical is an added advantage that variations in steam pressure or in degree of superheat during an operation do not interfere with the operation of the process and an extremely critical control of the operation is therefore not necessary.

It is another advantage of the present invention that the purity of the acrylonitrile recovered by steam distillation is high and more than adequate for reuse in the cyanoethylation process. It is also possible to utilize the principles of the present invention by steam distilling or stripping acrylonitrile out of the cyanoethylation mixture, after neutralization but without draining off the aqueous mixture. In some types of equipment such as the package kiers used extensively in the cyanoethylation of cotton yarn the nature of the equipment does not lend itself readily to the steam distillation of acrylonitrile

from the crude reaction mixture itself, and in such types of equipment it is preferable to drain off the neutralized reaction mixture and steam strip only the cyanoethylated cotton. Other types of equipment make steam distillation of the whole reaction mixture possible and therefore it is an advantage of the present invention that the principles can be used either to remove only the acrylonitrile which is in the cyanoethylated cotton or applied to the whole reaction mixture. The particular modification is determined by the nature of the equipment used in any particular operation.

The invention will be described in greater detail in conjunction with the specific example showing a typical application. The parts are by weight unless otherwise specified.

Cotton yarn in the form of yarn packages is cyanoethylated in a package dyeing kier by first introducing a dilute aqueous solution of caustic soda, for example about 2% and then reacting with an amount of acrylonitrile about 10 times the weight of the cotton at a temperature between 50–70° C. until cyanoethylation has proceeded to the desired degree which is determined by the nitrogen content of cyanoethylated cotton which should be between 2.5 and 6%. The reaction mixture is neutralized with phosphoric acid to a pH of about 5 to 6, then cooled down, and drained from the packages. Acrylonitrile is recovered from the drained reaction mixture in a distillation column by the normal procedure. Steam at 10 pounds p. s. i., slightly superheated, is introduced through the yarn steaming valve of the package dyeing machine and slowly passed through the packages finally passing to a condenser where both the water and volatilized acrylonitrile are condensed. The flow is maintained until substantially all of the acrylonitrile physically retained in the wet packages is removed.

The condensate is passed into a continuous decanting device as two layers, one of acrylonitrile containing water and the other water containing acrylonitrile, are formed when the process starts and the yarn packages contain the maximum amount of physically retained acrylonitrile. As the stripping proceeds the amount of acrylonitrile coming off per part of steam decreases; finally the amount of acrylonitrile becomes insufficient to form two layers. At this point the condensate is lead to the distillation column in which the drained reaction mixture is being treated. The introduction is part way up the column at a point corresponding to the averageacrylonitrile content of the material. The total amount of steam used both at passing to the decanter at the start and to the distillation column near the finish amounts to 12 parts of steam per part of acrylonitrile removed compared with 28 parts of steam per part of acrylonitrile by water washing.

It should be noted that a very large part of the acrylonitrile contained in the packages is recovered in the decanter and only a relatively smaller part passes to the distillation column. Since the handling losses in the decanter are relatively low, a minimum overall loss of

acrylonitrile results. The water layer from the decanter is introduced into the still together with the drained reaction medium but again at a different point in the column namely, a lower point corresponding to the composition.

In the foregoing example phosphoric acid has been described as the acid used in neutralizing the caustic soda. This acid is a very satisfactory one to use but the invention is in no sense limited thereto. It is equally possible to use sulfuric acid, acetic acid, and others. A mixture of sulfuric and phosphoric acid presents some advantages from a cost standpoint. Acids which are volatile such as acetic acid are somewhat less desirable particularly if the neutralization is carried to lower pH's as the acid may be volatilized in the distillation column contaminating the product.

We claim:

1. A process of recovering acrylonitrile from a reaction mixture for the cyanoethylation of cellulose using a strong alkali as a catalyst which comprises neutralizing the mixture until alkalinity due to strong alkali is at least substantially destroyed and removing acrylonitrile by steam distillation.

2. A process according to claim 1 in which after the neutralization of the reaction mixture with acid a major portion of the reaction mixture is drained from the cyanoethylated cellulose and steam distillation is effected only on the portion of the neutralized reaction mixture physically retained by the cyanoethylated cellulose.

3. A process according to claim 2 in which the cyanoethylated cellulose is cyanoethylated cotton.

4. A process according to claim 3 in which the cyanoethylated cotton is in the form of packages of cotton yarn.

5. A process according to claim 1 in which after neutralization with acid the cyanoethylation mixture is drained, recovering acrylonitrile therefrom by fractional distillation in a column, steam distilling acrylonitrile from the cyanoethylation mixture physically retained by the cyanoethylated cellulose, condensing the steam distillate as long as the acrylonitrile content thereof is sufficiently high to form two layers, separating the layers, recovering acrylonitrile from the aqueous layer by distillation, and passing the steam distillate, after the amount of acrylonitrile has reached a point sufficiently low so that a separate acrylonitrile phase cannot be produced, into the still in which the drained neutralized cyanoethylation mixture is being distilled.

6. A process according to claim 5 in which the cellulose is cotton.

7. A process according to claim 6 in which the cyanoethylated cotton is in the form of packages of cotton yarn.

8. A process according to claim 1 in which the neutralization is carried out with an acidic mixture comprising phosphoric acid to a pH of 5 to 6.

9. A process according to claim 8 in which the cyanoethylated cellulose is cyanoethylated cotton.

No references cited.