This invention relates to the manufacture of nicotinic acid by the oxidation of nicotine with nitric acid.

Nicotinic acid has become of increasing commercial importance because the human body can synthesize one of the constituents of the vitamin B complex from it. The cheapest and most readily available source of nicotinic acid is the nicotine in waste tobacco products, but the conversion process is rather cumbersome. Nicotine may be oxidized with nitric acid to nicotinic acid nitrate and the latter converted to nicotinic acid. The present invention relates to that part of the process in which the nicotine is oxidized to nicotinic acid nitrate.

In an ordinary commercial process of oxidizing nicotine to nicotinic acid using nitric acid as the oxidizing agent, the nicotine is dissolved in dilute nitric acid and more nitric acid of about 50% concentration is heated to about 95-100°C in a large, separate reaction vessel. The reaction vessel is then heated for a long period, usually about 20 hours, to evaporate substantially all the remaining liquid. Sufficient cold water is then added to dissolve the nicotinic acid nitrate residue and this solution is then taken to other apparatus in which the nicotinic acid is purified and converted to nicotinic acid.

An examination of the reactions by which nicotine is generally believed to be oxidized to nicotinic acid indicates that 29 mols of nitric acid are required to oxidize each mol of nicotine. Another mol of nitric acid is needed to dissolve the nicotine as nitric acid. These ratios are adhered to in commercial practice, even to the extent of adding an excess of nitric acid over the amount indicated by these ratios to insure complete reaction. Accordingly in usual commercial practice from 30 to 31 or more mols of nitric acid for each mol of nicotine are always present in the reaction vessel.

The use of such a tremendous amount of nitric acid for such a relatively small amount of nicotine presents a serious drawback to the use of the process, particularly from a commercial point of view. First, the reaction vessel itself must be large in order to handle the volume of the necessary acid. Then the time required to evaporate the large amount of liquid is considerable, as pointed out the usual practice taking around 20 hours. Furthermore, during the reaction period and the subsequent period during which the liquid remaining in the reaction vessel is evaporated, heavy, reddish-brown fumes are given off. They represent a very appreciable amount of nitric acid and an extensive apparatus must be provided to convert them back into the acid. As an overall result, a great deal of expensive equipment is required to produce a fixed amount of product.

In general, the present invention comprises the successful oxidation of nicotine to nicotinic acid using about 12 to 16 mols of nitric acid per mol of nicotine instead of 30 or more mols of nitric acid as in the ordinary practice of the process. The exact mechanism by which this unexpected result is obtained is not fully understood and the invention is not meant to be limited to any particular theory of action. Even more surprising is the fact that in most cases a somewhat higher yield is obtained using the reduced amount of acid. This is exactly contrary to the usual decrease in yield experienced in similar cases when a reduction in the proportions between the reactants is made.

The exact amount of acid which must be used is apparently not a definitely fixed figure. When a molar ratio of less than 9:1 is used the extent to which the oxidation reaction is completed begins to decrease quite appreciably. On the other hand, there appears to be no particular advantage in using a molar ratio greater than 16:1 so far as the yield produced is concerned. The optimum ratio appears to be from 12-15:1 although if necessity requires a smaller amount may be used.

Nor does the concentration of the nitric acid used appear to be particularly critical. As pointed out above, the usual commercial practice is to use acid having a concentration of about 50%. We have found that equally good results may be obtained using acid of much higher concentration. Because the more highly concentrated acid permits the feeding of greater charge of nicotine to a fixed size of reaction vessel there is a distinct advantage in using as strong an acid as possible. Economic considerations and physical handling difficulties however, place the optimum strength of acid at about 70% although even stronger acids may be used if it is found desirable to do so.

From a practical standpoint, the use of this reduced amount of acid has a great many advantages. The capacity of any existing apparatus can be more than doubled since one of the physical limitations on the apparatus was the size of the necessary reaction vessel. Because there is a smaller amount of acid present, the evaporating...
tion can be carried out in a much shorter length of time, thus freeing the apparatus for a second batch much more quickly. In addition, because a very much smaller amount of acid is being evaporated, the absorption system or other nitric acid recovery system need not be as large as in the case where the conventional practice is being carried out.

The invention will be described in greater detail in conjunction with the following specific examples, which are merely illustrative and not meant to limit the invention. The parts are by weight.

**Example 1**

1800 parts of 70% nitric acid were heated to 95° C. and a cold solution of 150 parts of nicotine in 100 parts of 70% nitric acid and 160 parts of water was slowly stirred into the hot acid at such a rate that 3½ hours were required. The overall molar ratio of nicotine to nitric acid was then 31:1. The temperature was maintained at 87° C., and a slow stream of air was blown over the surface of the heated and stirred liquid until it had been concentrated to the point where crystals of nicotinic acid nitrate began to separate. At this point the residue was diluted with 350 parts of cold water and heated to 60° C. to give a clear solution which was analyzed for nicotinic acid. There was present 91 parts of nicotinic acid or 80% of the theoretical yield.

**Example 2**

The same procedure as in Example 1 was carried out except that instead of 1800 parts of 70% nitric acid, only 850 parts (15:1 molar ratio) were used. Analysis proved that there were present 95 parts of nicotinic acid, or 84% of the theoretical yield.

We claim:

1. In the manufacture of nicotinic acid by oxidizing nicotine nitrate with nitric acid to nicotinic acid nitrate and converting the latter to nicotinic acid; the improvement which comprises adding an aqueous solution of nicotinic nitrate to from about 9 to 16 parts of strong nitric acid per mol part of nicotine nitrate, said nitric acid being free from other oxidizing compounds, and heating the mixture at from about 90° to 110° C. without adding any further additional oxidizing compounds while blowing a slow stream of air across the surface of the mixture being heated.

2. In the manufacture of nicotinic acid by oxidizing nicotine nitrate with nitric acid to nicotinic acid nitrate and converting the latter to nicotinic acid; the improvement which comprises adding an aqueous solution of nicotine nitrate to from about 9 to 16 parts of 70% nitric acid per mol part of nicotine nitrate, said nitric acid being free from other oxidizing compounds, and heating the mixture at from about 90° to 110° C. without adding any further additional oxidizing compounds while blowing a slow stream of air across the surface of the mixture being heated.

3. In the manufacture of nicotinic acid by oxidizing nicotine nitrate with nitric acid to nicotinic acid nitrate and converting the latter to nicotinic acid; the improvement which comprises adding an aqueous solution of nicotine nitrate to 15 parts of 70% nitric acid per mol part of nicotine nitrate, said nitric acid being free from other oxidizing compounds, and heating the mixture at from about 90° to 110° C. without adding any further additional oxidizing compounds while blowing a slow stream of air across the surface of the mixture being heated.

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