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PRODUCTION OF ALKYL NITRATES

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The present invention is concerned with a method of purifying volatile liquid nitric esters of monohydric alcohols and is particularly concerned with a method of purifying volatile liquid nitric esters of monohydric aliphatic alcohols obtained by distillation as from the products of an esterification reaction between the corresponding aliphatic alcohol and nitric acid, especially when the esterification is conducted with aqueous nitric acid in the presence of urea.

In the preparation of liquid nitric esters of the lower aliphatic alcohols by distillation it is usual to wash the crude liquid nitric ester-containing portion of the condensate from the distillation with water and subsequently with a mildly alkaline solution in order to remove any nitric acid and monohydric aliphatic alcohol present in it.

For certain of the aforesaid liquid nitric esters prepared in this way it is found that even after the water and mildly alkaline washings the liquid nitric ester, although not affecting stainless steel, rapidly and progressively corrodes ordinary ferrous metals such as mild steel, cast iron and galvanised iron, with the production of a rusty deposit that readily flakes away from the metal. This corrosive action proceeds even when air is excluded and when the ferrous metal is totally immersed in the liquid nitric ester. Such corrosive samples of the aforesaid liquid nitric esters also attack copper and its alloys with the formation of a blue coating that adheres to the metal surface and they also attack aluminum slightly. It will be readily understood that these corrosive properties cause much inconvenience in the storage and transport of the liquid nitric ester and also in connection with its industrial utilisation, for example as a fuel burning alone or in presence of oxygen, or as an additive to an oil fuel, since a liquid nitric ester exhibiting these properties cannot be stored or handled in conventional ferrous metal containers and cannot be passed through narrow passages, e.g. for spraying, especially in ordinary ferrous metal or copper alloy structures. These corrosive properties have been found to be shown particularly by the volatile liquid nitric esters of monohydric alcohols having at least one methyl group close to the nitrate group as for instance ethyl nitrate, isopropyl nitrate, and secondary butyl nitrate. There is furthermore evidence that variations in the conditions of an esterification have an effect on the corrosive properties of the resulting volatile liquid nitric ester obtained by distillation from the products of the esterification reaction.

This corrosive effect is very easily shown on a piece of mild steel wholly immersed in the liquid nitric esters in a glass container as the piece of mild steel develops a visible rust coating within 24 hours which increases in amount with increasing time of exposure leading to the deposition of rusty particles at the bottom of the container. The effect has been observed most strongly with isopropyl nitrate and in lesser but still objectionable degree with ethyl nitrate, with secondary butyl nitrate, and with ethoxy-ethyl nitrate prepared by nitration of the corresponding alcohols with aqueous nitric acid in the presence of urea. Thus in the direct nitration method for the

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production of isopropyl nitrate from isopropyl alcohol, aqueous nitric acid and urea, there is distilled and condensed from the reaction mixture a mixture containing isopropyl nitrate, aqueous nitric acid and isopropyl alcohol, which separates out into a layer rich in isopropyl nitrate and a layer rich in water. The isopropyl nitrate-rich layer is separated and washed with water, which has the effect of removing isopropyl alcohol from it and diminishing its acidity. Even after water-washing, however, the isopropyl nitrate quickly develops acidity and it is found that mild steel drums and galvanised iron drums are severely attacked by the product and aluminium containers are also somewhat corroded by it, while copper pipes acquire a blue bloom when it is passed through them.

It might be supposed that the residual acidity and corrosive properties of the product would easily be removed by washing the separated isopropyl nitrate with a dilute solution of a mild alkali such as sodium carbonate, but this does not occur for on separation from the alkaline solution and on standing the isopropyl nitrate is found to be still harmful to the aforementioned metal vessels and its acidity may even exceed that left after simple water-washing.

These corrosive properties of the aforesaid volatile liquid nitric esters and the associated development of acidity after washing are not inherent properties of the volatile liquid nitric ester that exhibits them. We have discovered that the corrosive properties and the acidity that develops in the water or dilute alkali washed volatile liquid nitric ester are due to the presence therein of an impurity consisting of a more readily hydrolysable ester than said nitric ester and formed as a result of the particular method of preparation of the nitric ester. The impurity is found to be the nitrous ester of the monohydric aliphatic alcohol and to be formed in the main in the gaseous phase during the distillation stage of the products of the esterification reaction between the corresponding alcohol and nitric acid.

When a volatile liquid nitric ester of a monohydric aliphatic alcohol contaminated with the corresponding nitrous ester as an impurity is washed so that substantially all free nitric acid associated with it is removed, e.g. by washing it with water and then with dilute alkali, and the ester is separated from the aqueous washing medium, hydrolysis of the nitrous ester continues slowly in the presence of the water present in the dissolved state in the product, and the acid products of hydrolysis so generated give rise to the attack on the metals.

It has now been found that a volatile liquid nitric ester of a monohydric aliphatic alcohol exhibiting these corrosive properties when washed in the aforesaid manner, and containing the corresponding nitrous ester as an impurity, can be rendered substantially free from said nitrous esters and can thus be prevented from developing corrosive properties, if the crude nitric ester is first washed with an excess of an aqueous solution containing urea and a mineral acid in a concentration to cause evolution of gas in the presence of the urea only as long as any nitrous ester is present and if the so treated nitric ester is substantially freed from the acid used and excess of urea, as by treatment with water and a metallic carbonate or hydroxide or the like neutralising agent.

According to the present invention the method of purifying volatile liquid nitric esters of monohydric aliphatic alcohols substantially from nitrous ester comprises washing the nitric ester with an excess of an aqueous solution containing urea and a mineral acid in a concentration to cause evolution of gas in the presence of the urea only as long as any nitrous ester is present and thereafter freeing the nitric ester substantially from said acid and excess urea.

To be sure that sufficient urea is employed the percentage of the nitrous ester present in the volatile liquid nitric ester of the monohydric aliphatic alcohol may if desired be determined analytically as by a suitable titration method. In the absence of the mineral acid the rate of evolution of gas is quite imperceptible and it may be supposed that the function of the mineral acid is to accelerate hydrolysis of the nitrous ester into the monohydric alcohol and nitrous acid, the nitrous acid then reacting immediately in known manner with the urea in the molar ratio 2 : 1 to produce nitrogen, water and carbon dioxide, the destruction of the nitrous acid causing the hydrolysis to proceed progressively until the nitrous ester is used up and the gas evolution consequently ceases. The mineral acid concentration must therefore be sufficient to cause the evolution of the gas to take place at a visible rate so that the treatment can be completed within a reasonable time. On the other hand, the mineral acid concentration must not be sufficient to bring about any substantial hydrolysis of the volatile liquid nitric ester, for this would not only result in the loss of the desired material but would also result in the consumption of urea in greater amount than that required for the nitrous acid resulting from hydrolysis of the nitrous ester, so that the gas evolution would never stop, and would ultimately result in the consumption of the whole of the urea so that the reaction would become violent.

Nitric acid may conveniently be employed as the mineral acid and it is preferred that the acid concentrations of the aqueous solution in contact with the alkyl nitrate should be between approximately 1 and 3 Normal, since these concentrations suitably accelerate the hydrolysis of the nitrous ester without resulting in any appreciable hydrolysis of the nitric ester. It is possible to employ the urea and the mineral acid in the form of the urea salt of the acid, since urea salts dissociate satisfactorily in water, and it is especially desirable to use urea nitrate since this compound crystallises out on cooling from the waste nitric acid formed in processes for the manufacture of the volatile liquid nitric esters of aliphatic alcohols when these alcohols are treated with nitric acid in the presence of urea, for example in continuous processes where a portion of the liquid reaction mixture from which said nitric ester is distilled is run to waste. It is convenient to use a nearly saturated solution of urea nitrate in water. It is thus an advantage of the invention that it can be carried out with a material available as a by-product in the production of the nitric ester to be purified.

The treatment may advantageously be conducted by washing the impure volatile liquid nitric ester with the solution containing the urea and the mineral acid under such conditions as to enlarge the surface of contact between the two immiscible liquids, for example with mechanical agitation or agitation by means of an air stirrer, the action of which is discontinued when it is desired to observe the progress of the evolution of gas. The washing may advantageously be conducted at a temperature somewhat above atmospheric, e.g. at about 40° C., since this accelerates the destruction of the nitrous ester without materially affecting the nitric ester, but the reaction also occurs satisfactorily at room temperature. It is usually desirable that the crude volatile liquid nitric ester of a lower monohydric aliphatic alcohol should be subjected to a water washing before the treatment is commenced.

Whatever may be the mechanism of the reaction between the impure volatile liquid nitric ester of the monohydric aliphatic alcohol and the aqueous solution containing the urea and the mineral acid, the fact is that nitrogen and carbon dioxide are evolved and the nitric ester soon attains a condition in which after water washing and separation from the wash water its acidity no longer increases on storage and it can be stored for example in mild steel drums without damaging them.

The invention is illustrated in the following examples.

Example 1

Isopropanol is nitrated in a continuous manner by introducing continuously separate streams of 75% isopropanol containing 10% added urea and of 70% nitric acid into a nitration reaction mixture of 40% aqueous nitric acid containing urea in a nitrator in which the level of the liquid is kept constant by a constant level overflow and by distilling and condensing the volatile products so formed. The condensate consists of two layers. The lower layer is impure isopropyl nitrate and is washed with two volumes of water to remove unreacted isopropanol. The amount of isopropyl nitrite in the water washed isopropyl nitrate is obtained by determining the specific gravity of the dried water washed product and by making use of a graph which records the specific gravities for pure isopropyl nitrate, pure isopropyl nitrite and mixtures of isopropyl nitrate and isopropyl nitrite of known composition.

After the isopropyl nitrite content is determined the water washed product is thoroughly shaken for 20 minutes with its own volume of a solution of urea nitrate in water of such concentration that it is saturated at room temperature. This solution contains a considerable excess of urea nitrate over that amount required to destroy completely the isopropyl nitrite present in the impure isopropyl nitrate. This solution is also easy to prepare and is convenient to handle. The solubility of urea nitrate in water at room temperature is approximately 12% by weight. The resulting mixture is allowed to separate into two layers whereof the upper layer consisting of isopropyl nitrate is separated off and washed with twice its own volume of water in which it sinks.

The resulting lower layer of isopropyl nitrate is carefully separated from the supernatant wash water. Its acidity calculated as nitric acid is 0.005% and it is found that this acidity does not increase on standing. The product can be stored in a mild steel drum for more than 6 months without effecting any noticeable corrosion. In a comparative test in which the isopropyl nitrate rich layer of the condensate is washed directly with water instead of with urea nitrate, it is found impossible to reduce the acidity of the isopropyl nitrate layer below about 0.15%. After a week's storage in a mild steel container the resulting isopropyl nitrate causes relatively severe corrosion of the container. If the isopropyl nitrate layer of the crude condensate is washed with dilute sodium carbonate solution instead of water its acidity after a short storage is not less than that which is obtained as a result of water washing and the product which is separated from the dilute alkaline liquor similarly corrodes a mild steel drum.

Example 2

Impure isopropyl nitrate, prepared as in Example 1, and exhibiting visibly corrosive properties on mild steel test pieces immersed in it within one hour even in the dark is washed with an equal volume of an aqueous solution of urea and nitric acid in which the nitric acid concentration is approximately normal and the molar ratio of urea to nitric acid is approximately 2:1. The washing is conducted at 40° C. with mechanical agitation until the evolution of colourless gas which begins at a rate sufficient to cause the mixture to froth, is no longer visible. This takes about twenty minutes. The stirring is stopped and the ester layer, the denser one, is separated from the aqueous layer which is found still to contain urea in solution, and is washed with twice its own volume of water. After the ester is separated from the wash water it is filtered through a column of marble chips. Test pieces of mild steel when immersed in the resulting product in the dark undergo no visible tarnishing or corrosion over two weeks' time.

Example 3

The ethyl nitrate-rich layer which is separated in the condensed distillate in the production of ethyl nitrate

with aqueous nitric acid in presence of urea is treated with its own volume of a saturated solution of urea nitrate and is separated and washed in the same manner as the isopropyl nitrate-rich layer in Example 1. The resulting product is of negligible acidity and can be stored for 6 months in a mild steel drum without exerting disadvantageous corrosion, whereas a sample of the same ethyl nitrate-rich layer thoroughly washed with water instead of urea nitrate solution has a noticeable acidity and corrodes a mild steel container badly within a week.

Example 4

Secondary butyl nitrate prepared by distillation from aqueous nitric acid to which are added continuously separate streams of secondary butyl alcohol and nitric acid and exhibiting visibly corrosive properties on mild steel test-pieces immersed in it within twelve hours, is washed with an equal volume of an aqueous solution of urea nitrate of such concentration that it is approximately saturated at room temperature. The resulting mixture is allowed to separate into two layers, whereof the upper layer consisting of secondary butyl nitrate is separated off and washed with an equal volume of a solution of 2% sodium carbonate. Test-pieces of mild steel immersed in the resulting product after separation, undergo no visible tarnishing or corrosion over one week's time.

What we claim is:

1. A method of purifying volatile liquid nitric esters of monohydric alkyl alcohols substantially from nitrous ester which comprises washing the nitric ester with an excess of an aqueous solution containing urea and nitric acid in a concentration sufficient to cause visible evolution of gas in the presence of the urea only as long as the nitrous ester is present but not sufficient to cause any substantial hydrolysis of the liquid nitric esters, and there-

after freeing the nitric ester substantially from said acid and excess urea.

2. A method as claimed in claim 1 wherein the acid concentration of the aqueous solution in contact with the alkyl nitrate is between approximately 1 and 3 Normal.

3. A method as claimed in claim 1 wherein the urea and the nitric acid are in the form of the urea salt of the acid.

4. A method as claimed in claim 1 wherein the washing of the nitric ester with an excess of an aqueous solution containing urea and nitric acid is carried out at about 40° C.

5. A method as claimed in claim 1 wherein the nitric ester is subjected to water washing before washing it with an excess of an aqueous solution containing urea and nitric acid.

6. In a method for preparing a purified noncorrosive volatile liquid nitric ester of a monohydric alkyl alcohol by reacting said alcohol with nitric acid and distilling off the nitric ester thus formed, the improvement whereby nitrous ester formed in distilling off said nitric ester and admixed therewith to create a corrosive effect is removed, said improvement comprising the steps of washing the distilled nitric ester containing nitrous ester with a saturated aqueous solution of urea nitrate until said nitrous ester is substantially completely removed without substantial hydrolysis of said nitric ester and thereafter separating said nitric ester from said urea nitrate.

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