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MANUFACTURE OF PROPYL NITRATE

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This invention relates to a process for the nitration of monohydric alcohols. In particular, our invention relates to a process for the manufacture of propyl nitrate.

The nitrate esters of propyl alcohol are useful as ignition improvers and as chemical intermediates.

Heretofore, there has been no process for propyl nitrate manufacture which was suitable for economical commercial operation.

Among the several difficulties attending the nitration of alcohols which prior processes have attempted to overcome is the ease with which the alcohols employed are consumed in side reactions by the nitrating mixture employed. Such side reactions not only decrease the yield of nitrate obtainable from the alcohol and decrease the quality of the product, but may be so extensive as to cause the reaction to become uncontrollable and hazardous. Among the remedies proposed for offsetting such side reactions are the addition of considerable quantities of urea, operation at extremely low temperatures, continuous distillation of the product with water or at low pressures, or a combination of these devices. All these methods are costly, and result in additional disadvantages such as elaborate process equipment, slow reaction and impure product.

Propyl nitrates can be considered as monopropellants, and, therefore, their production by direct nitration by prior processes of propyl alcohol is attendant with considerable risk because of the high order of reactivity of the alcohols in the presence of oxidizing agents and the reactivity of the products. Therefore, the use of methods and processes previously disclosed in the art have not been entirely satisfactory when applied to the manufacture of propyl nitrate.

Many prior processes for the nitration of alcohols specify mixtures of nitrating agents intended to control the reaction. The use of mixtures of sulfuric acid and nitric acids is the most common practice in the nitration art, but heretofore the use of sulfuric acid, as in "mixed acid," has led to two serious complications. In the first instance the activating effect of the sulfuric acid has been such that it was always necessary to employ one or more of the devices enumerated above to moderate the reaction. In the second instance the use of such mixed acids has resulted in a reaction mixture from which the product can be recovered only with difficulty, because of high solubility and the formation of stable emulsions. Among the proposed remedies for this separation problem are dilution of the reaction mixture followed by an azeotropic distillation, and continuous distillation from the reactor of the product. Both of these remedies result in poor recoveries of alkyl nitrate, either through decomposition or solubility effects, and further increase the cost of the materials so produced.

In addition to the inherent difficulties in the manufacture of alkyl nitrates by the direct nitration of alkyl alcohols described hereinbefore, prior processes proposing such nitration are not applicable to alcohols containing more than minor amounts of secondary alcohols. There-

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fore, to nitrate propyl alcohol by a process applicable to both primary and secondary isomers, such prior art processes cannot be employed. Furthermore, with the processes of the prior art it is indicated that the amount of nitric acid employed should not be above a small specified excess of that required to nitrate the alcohol.

In attempts to moderate the reactivity of the mixed acid and increase the separability of the reaction mixture, it has been proposed to employ large excesses of nitric acid. The separation problem is sufficiently great that further proposals have been made to sacrifice yield and fast reaction by using large excesses of nitric acid in the absence of sulfuric acid. However, when such nitrating mixtures are employed, the water formed as a by-product so retards the esterification reaction that the oxidation reaction becomes significant, and a commercially successful operation cannot be achieved. In order to speed the desired reaction under such conditions, it has been proposed that the nitrating mixture be fortified during the nitration with fresh or recovered nitric acid. This operation is wasteful of nitric acid and requires an elaborate recovery system. Furthermore, in processes wherein large excesses of nitric acid are employed the nitrate ester requires further treatment to render it stable on storage.

It is, therefore, an object of our invention to provide a process for the nitration of propyl alcohol which overcomes these and other disadvantages of the prior art and which can be applied to the nitration of both isomeric forms. Furthermore, it is an object of the instant invention to provide a process for the manufacture of propyl nitrate by a method wherein moderate temperatures are employed and which can be adapted to a continuous operation. It is a further object of this invention to provide an easily recoverable propyl nitrate product of high purity and stability. An additional object of this invention is to provide a process for the nitration of propyl alcohol under conditions whereby it is unnecessary to recover nitric acid and whereby a minimum amount of sulfuric acid is required. Our invention further provides a safe nitration process wherein it is unnecessary to quench, drown, or otherwise interrupt the reaction before its completion, and wherein costly chemical modifiers are not required. Still further objects of our invention will be apparent from the further description of our process hereinafter.

According to the present invention, propyl alcohol is nitrated at a temperature between about -8° C. and about 10° C. with mixed nitric-sulfuric acid such that the spent acid contains at least 74 per cent by weight of sulfuric acid by employing a mixed acid containing 0 to 14 weight per cent water and 50 to 68 weight per cent sulfuric acid. These conditions determine the concentration of nitric acid which can be employed. In our process we maintain an excess of nitric acid. We have found that it is necessary to employ an excess of nitric acid, but that the amount of such an excess is not critical. Our process is applicable to n-propyl alcohol, isopropyl alcohol, and to mixtures thereof. When we use n-propyl alcohol, we prefer to operate in the temperature range of about -8° C. to about 10° C., and with isopropyl alcohol, in the range of about -8° C. to about 0° C. The preferred temperatures for the nitration of mixtures of the two alcohols vary with the percentage of isopropyl alcohol in the particular mixture to be nitrated. With concentrations of isopropyl alcohol up to about 20 per cent, temperatures up to about 8 or 9° C. may be employed; but when the percentage of isopropyl alcohol is much greater than 20 per cent, the temperature should not be allowed to greatly exceed about 5° C.

By employing sulfuric acid in concentrations between 50 and 68 weight per cent and with not more than 14

per cent by weight of water, we have found that the water present in the final esterification mixture can be adequately bound by the sulfuric acid. Therefore, the esterification reaction occurs at a rapid rate, oxidation by nitric acid is essentially eliminated, and urea or other chemical modifier is unnecessary. However, we have found that if the amount of nitric acid employed is below the amount required to nitrate the alcohol, that is, if the amount of nitric acid employed is less than a stoichiometric amount, oxidation reactions occur. Thus, we prefer an excess of nitric acid to alcohol. All acid compositions and proportions of mixed acid to alcohol within this range are satisfactory, provided the molar ratio of water to sulfuric acid in the spent acid is not more than 1.9 to 1, or 0.35 part by weight of water per part of sulfuric acid, and the above defined ranges determine the proportions of the reactants.

Although the reaction proceeds smoothly with mixed acid containing somewhat less than 20 per cent nitric acid, the separation of the product from the spent acid is complicated, since propyl nitrate is somewhat soluble in concentrated sulfuric acid solutions.

The reaction mixture of our invention is chemically stable; that is, the proportions of reactants are such that after reaction has occurred, the reaction products can be separated without recourse to the expedients of prior processes. Thus, we need not employ urea to decompose nitric oxides, or to stop the reaction by sudden dilution with water, ice, and the like.

In the manufacture of propyl nitrate we have found that there is a greater separation problem than in the manufacture of certain other alkyl nitrates. One method of overcoming this separation problem is to employ a recycle of spent acid. Because of the relative instability of the reactants, it would be expected that such a recycle process would be inherently dangerous, but, surprisingly, we find that we can increase the yield by employing such recycle techniques in an efficient and safe manner. We can, however, operate safely without recycle at the expense of our improved yield.

We prefer to employ our process as a continuous operation, because of the significant economies inherent in such a method. However, because of the stability of the reaction mixture as described above, a batch operation can be conducted without introducing other complications. In a continuous operation, the residence time, or contact time, of reactants and products can, as noted above, be as long as desired. The minimum duration of the residence time has never been determined, and it is dependent solely upon the heat removing capacity available and upon the facilities for handling the liquid materials. For example, we have achieved successful operation with a residence time as high as 15 minutes, and as little as 0.6 minute or lower. For a commercial process this factor is extremely significant, for the desired production capacity can be varied over wide limits in a single reaction and recovery system, merely by controlling the flow of reactants and coolant. Thus, our process is extremely flexible.

The size of the reactor employed in our process in relation to the output capacity is primarily dependent on the provisions for agitation and cooling; that is, at a given throughput the size of the reactor controls the residence or contact time. As stated above, the minimum contact time is not critical, so that the body of the reaction mixture functions primarily as a means for dispersing the reaction heat. Therefore, the quantity of such reaction mixture at a given throughput required to maintain the desired temperature depends solely on the means supplied for removing the reaction heat and not on the reaction time requirements.

The method of addition of the reactants in our process is not critical. For a smooth continuous operation we prefer to add the acid and alcohol continuously at a steady rate, although for some purposes intermittent

addition of one or more streams may be desired. It is not essential that the sulfuric and nitric acids be premixed before introduction to the reactor, although we prefer this method of addition in order to minimize the mixing requirements imposed on the reactor agitator, and to remove the heat of mixing prior to conducting the nitration reaction. Likewise, it is not necessary to precool the liquid reactants before introduction to the reactor. For example, at a low or medium output from a given reactor system the alcohol and acid may be introduced at or near the prevailing atmospheric temperature and maintain at all times a controlled, efficient reaction. At high outputs it may be desirable to precool one or more of the reactants to reduce the heat transfer requirements of the cooling system in the reaction zone.

One preferred method of introducing the reactants to the reactor system is to add separately the alcohol and the mixed acid as a steady stream to the stirred reaction mixture, such that the streams are delivered near the surface of the liquid. Alternatively, either or both of these streams may be delivered below the surface of the liquid at any desired depth, either in a single stream, a jet impinging on the agitator, or as dispersed droplets. We prefer to maintain the two liquid phases of the reaction mixture; that is, the phase consisting predominantly of alkyl nitrate and the phase consisting predominantly of spent acid, in a fine dispersion, rather than as two distinct layers. Thus, heat transfer is facilitated and the development of local zones of high temperature is avoided.

To recover the nitrate product from the process of our invention we prefer to continuously deliver the reaction mixture to a settling chamber, permit the layers to separate by gravity, and continuously withdraw from such settling chamber the upper product layer and the lower spent acid layer. Other methods of separation can also be employed without departing from the scope of our invention; for example, continuous centrifugation, solvent extraction or distillation. It is, however, a feature of our invention that such costly operations are not required to obtain a commercially acceptable pure product. It is a special feature of our process that urea is not required in the reaction mixture, as urea reacts with nitric acid to yield gaseous products which contribute to the tendency of prior processes to form more or less stable emulsions, a major factor in complicating the separation step and reducing the yield. By the above described separation method a product is obtained which may have a cloudy appearance, due to a trace of dispersed aqueous acid phase. This can be removed, to produce a clear product by several conventional methods. We prefer to first wash the crude product with aqueous soda ash to neutralize the traces of dispersed spent acid, and then percolate the product through a tower containing a solid adsorbent, such as Filtrol, silica gel, alumina, or calcium chloride to remove the moisture present. A second advantage of this step is that occasionally a straw-colored product is obtained which is made substantially water-white by such treatment. The product obtained by our process contains about 99 per cent alkyl nitrate.

By the above described treatment the alkyl nitrate product is obtained in high yield, of the order of 70 per cent of the alcohol introduced to the reactor. This excellent yield can be further increased if a small amount of water or ice is added to the reaction mixture before passing to the settler. This water need not exceed about 5 per cent by volume of the total reaction mixture.

The process of our invention can be further understood by reference to the following example which illustrates the nitration of n-propyl alcohol, isopropyl alcohol, and mixtures of the two alcohols. Unless stated otherwise, in the example that follows all percentages and parts are by weight.

Example

To a stainless steel open reactor equipped with an efficient agitator, internal cooling coil, and means for

temperature measurement, a continuous stream of n-propyl alcohol was introduced below the surface of the agitated liquid, and mixed acid was continuously introduced at a point about one-third the depth of the agitated liquid. The reactor was further provided with an overflow tube, by means of which the liquid level was maintained constant. The mixed acid composition was 20 per cent nitric acid, 68 per cent sulfuric acid, and 12 per cent water. The reaction mixture was maintained at a temperature of 0° C. to 5° C. The dispersed reaction mixture was continuously discharged by overflow into a separator tank containing a simple one-plate baffle, a cooling coil, an overflow line for the upper layer, and a discharge line for the lower layer. The upper product layer overflowed into a vessel equipped with an agitator and a delivery line for addition of 10 per cent sodium carbonate solution, and a discharge line to a second separator. The upper stratum from the second separator overflowed continuously to the top of a Filtrrol-packed tower. The product was withdrawn continuously from the bottom of this tower. During one hour's operation, 1856 parts of mixed acid and 289 parts of n-propyl alcohol were fed to the reactor. The yield of n-propyl nitrate during this period of time was 464 parts or a percentage yield of 66.5 per cent. The quantity of mixed acid used contained 5 per cent excess nitric acid over that required to completely esterify the alcohol present in the feed. Contact time of the material in the reactor was three minutes.

When the above procedure is carried out at temperatures varying from -8° C. to 10° C. substantially identical results are obtained. Similar results are obtained when mixed acid containing as little as 60 per cent sulfuric acid and up to 14 per cent water is utilized.

When we apply the procedures described in the example to pure isopropyl alcohol, we find that by controlling the reaction temperature at between about -4° C. and 0° C., we obtain a good yield of isopropyl nitrate of a purity suitable for all commercial processes. Moreover, we can obtain comparable results by employing temperatures in the order of between about -8° C. and -4° C. In addition, by varying the proportions of the nitrating agent mixtures within the limits of the present invention described hereinbefore, we can effect a good yield of isopropyl nitrate of the same purity and quality.

We have found that, in general, when we employ the procedure described in the example to a mixture of the isomeric forms of propyl alcohol containing a major proportion of n-propyl alcohol, we obtain a good yield of the isomeric propyl nitrates of a purity suitable for all commercial processes. Thus, for example, when we use as the feed alcohol a mixture comprising about 80 per cent n-propyl alcohol and 20 per cent isopropyl alcohol and subject this mixture to the procedure described in the example at a temperature of 7° C., we obtain a good yield of mixed propyl nitrates of high purity and quality. Likewise, when we use as the feed alcohol other mixtures containing a major proportion of n-propyl alcohol; that is, when the amount of n-propyl alcohol is present in an

amount exceeding 50 per cent by weight, such as for example, a mixture of about 70 per cent n-propyl alcohol and 30 per cent of isopropyl alcohol, and subject such mixtures to the procedure described in the example at a temperature of 4° C., we obtain a good yield of mixed propyl nitrates of high purity and quality.

We have found that, in general, when we employ the procedure described in the example to a mixture of the isomeric forms of propyl alcohol containing a major proportion of isopropyl alcohol, we obtain a good yield of the isomeric propyl nitrates of a purity suitable for all commercial processes. Thus, for example, when we use as the feed alcohol a mixture comprising about 80 per cent isopropyl alcohol and 20 per cent n-propyl alcohol and subject this mixture to the procedure described in the example, we obtain a good yield of mixed propyl nitrates of high purity and quality when utilizing temperatures between -8° C. and 1° C. Likewise, when we use as the feed alcohol other mixtures containing a major proportion of isopropyl alcohol; that is, when the amount of isopropyl alcohol is present in an amount exceeding 50 per cent by weight such as, for example, a mixture of about 70 per cent isopropyl alcohol and 30 per cent n-propyl alcohol, and subject such mixtures to the procedure described in the example, we obtain a good yield of mixed propyl nitrates of high purity and quality when operating at temperatures between -8° C. and 3° C.

In addition, we have found that the contact time in any of the above and other processes of the instant invention can be extended over the range of 15 minutes to 0.6 minute without substantial alteration of the results obtained.

The foregoing example is not intended to limit the scope of our invention, as other embodiments will be apparent to those skilled in the art.

Having described the advantages of our invention, the need therefor, and the best methods for carrying it out, we do not intend that our invention be limited except within the scope of the appended claim.

We claim:

A process for the nitration of propyl alcohol comprising nitrating the propyl alcohol at a temperature between about -8° C. and 10° C. with a urea-free nitration mixture consisting essentially of nitric and sulfuric acids, the sulfuric acid in said mixture being at least about 50 per cent by weight, the water in said mixture being not more than 14 weight per cent, the amount of nitric acid in said mixture being at least equal to the stoichiometric requirement to substantially completely esterify said propyl alcohol, and the ratio by weight of water to sulfuric acid in the final esterification mixture being not more than 0.35 to 1.

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