

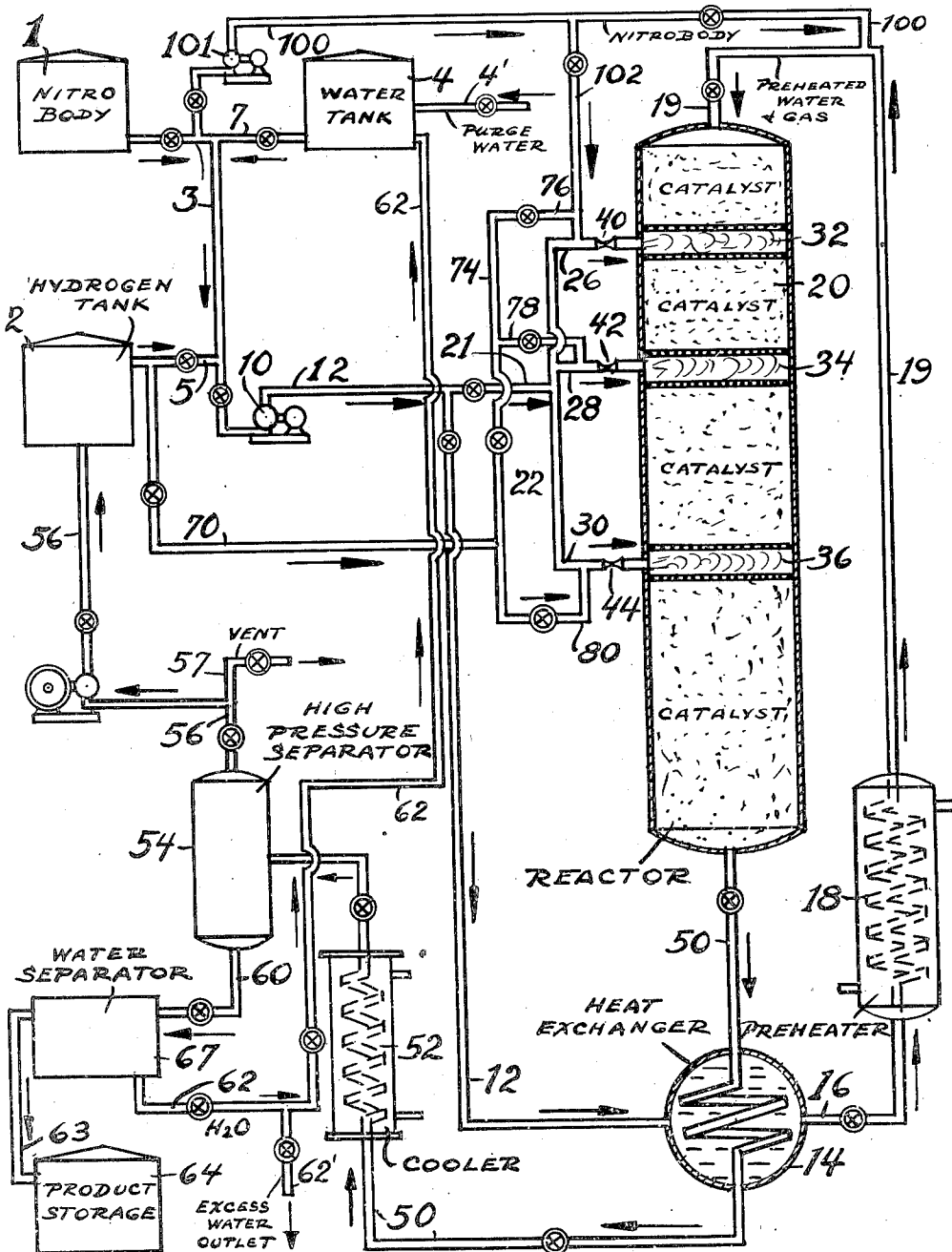
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TEMPERATURE CONTROL FOR HIGHLY EXOTHERMIC REACTIONS

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## TEMPERATURE CONTROL FOR HIGHLY EXOTHERMIC REACTIONS

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The present invention relates to improvement in the art of controlling the temperature of highly exothermic, chemical reactions, and more particularly it relates to the control of such temperatures by permitting a liquid to evaporate in a reaction zone under conditions such that the amount of liquid vaporized is increased by the addition of a gas adapted to absorb vapors from said liquid, as the temperature in the reaction zone increases, whereby such increase is counteracted by the cooling effect of the vaporizing liquid.

Our invention has general application but one important aspect of it has to do with the control of temperature during the reduction of nitro compounds to the corresponding amines. The production of aromatic amines has become important recently since these compounds when blended even in relatively small percentages in aviation gasoline materially improve the rich mixture performance of the gasoline. Stated otherwise, the addition of relatively small quantities of aromatic amines, such as xylidine, to an aviation gasoline greatly increases its capacity for power output which is, of course, a valuable characteristic of the aviation gasoline during take-off from the ground or during sudden acceleration in flight.

The commercial production of aromatic amines from the corresponding nitro aromatics has been carried out before our invention by the hydrogenation of the nitro aromatics but commercial application of this process by the conventional oil hydrogenation technique is difficult because of the two following factors:

(1) Aromatic nitro bodies are unstable at temperatures of the order of 600° F. and while the amines are more stable at these elevated temperatures, nevertheless, they decompose.

(2) The heat of reaction involved in the reduction of a nitro aromatic to the corresponding amine is very high.

It follows from the foregoing that a successful commercial operation for the production of amines by reduction of the corresponding nitro aromatics must embody means for rigid temperature control both from the standpoint of obtaining high yields of high quality material as well as safeguarding operating personnel and equipment. We have discovered means for insuring rigid temperature control and, broadly, these means involve utilizing liquid water and injecting cooling gas which expedients make it possible to hydrogenate nitro aromatics in commercial high pressure hydrogenation equipment. Thus we have invented a process for successfully reducing

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nitro aromatics on a commercial scale and operating at a pressure of from 500–5000 lbs. per square inch or higher, in the presence of a catalyst.

The main object of our present invention therefore is to conduct exothermic reactions at elevated temperatures and pressures under conditions of rigid temperature control.

A more specific object of our invention is to provide means for reducing nitro aromatics in the presence of a catalyst at elevated temperatures and high pressures while maintaining rigid temperature control at temperature levels insuring high quality and yields and, at the same time, safeguarding operating personnel and equipment.

Speaking generally at first, our new process involves the following general steps:

(1) Hydrogen, which may or may not be pure, and water at operating pressure are heated to the desired temperature level first by indirect heat exchange with the reaction products and second by forcing the mixture through a suitable heating means such as a fired coil. The nitro aromatic to be reduced is mixed with the preheated water-hydrogen mixture thereby reducing to a minimum the time at which the nitro aromatic is maintained at temperature in the absence of a catalyst.

The nitro aromatic may be injected into the preheated water-hydrogen stream in the pure form or as a mixture of the nitro aromatic and recycled amine product or other suitable diluent. Although we prefer to mix the nitro aromatic with the preheated water-hydrogen stream, the preheating operation may be conducted by first mixing the nitro aromatic with water and hydrogen at operating pressure and then heating first by indirect heat exchange with the reaction products and second by forcing the mixture through a suitable heating means such as a fired coil.

(2) The mixture enters the reaction chamber containing a suitable catalyst whereupon hydrogenation takes place with an evolution of heat which raises the temperature of the mixture. As previously indicated, we control the temperature at the desired level which is below 600° F., and preferably below 500° F., by maintaining at all times within the reaction zone an excess of a vaporizable liquid such as water, which water absorbs sensible heat and thereby increases in temperature, but more important, will absorb latent heat of vaporization depending upon the amount of gas present (i. e. hydrogen gas) and the temperature condition. Therefore with liquid water present (or some other vaporizable liquid) there is always available a very large latent heat ca-

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capacity which can be easily utilized by adding gas, such as cold circulating hydrogen gas to the reaction zone. The injected gas absorbs sensible heat thus lowering the reaction temperature and vaporization will take place up to the saturation point of the total gas present before the temperature of the reaction zone again rises. When the temperature in the reaction zone does again tend to increase, the saturation point is raised thus allowing more water to evaporate with a consequent control of the tendency of the reaction zone, generally, to increase in temperature.

(3) The products and residual gas pass through the heat exchanger previously mentioned, then flow through a cooler and eventually into a separator where the hydrogen is separated from the amine.

(4) The product is withdrawn from the high pressure separator, its pressure reduced usually in one or more stages down to normal pressure. The gas separated from the product in the high pressure separator is recycled, after mixing with fresh make-up hydrogen-containing gas, to the reaction zone.

In order to maintain the proper concentration of hydrogen it may be necessary to scrub the gas separated from the product or to vent a certain portion of it before mixing with the fresh make-up gas for the reason that impurities in the original hydrogen, such as methane, nitrogen, etc. will accumulate in the system. Of course, if pure hydrogen is used, this venting of a portion of the recycle gas will not be necessary.

In order to afford a better understanding of our invention, we have illustrated diagrammatically in the accompanying drawing a preferred modification of our invention.

Referring in detail to the drawing, we shall assume that it is desired to reduce mono-nitro-xylene to form xylydine, which mono-nitro-xylene is contained in the storage drum 1. In the storage drum 4 there is contained water which is to be mixed with hydrogen and the nitro xylene and fed therewith to a reaction zone. In the storage drum 2 fresh hydrogen-containing gas is contained. Water is withdrawn from storage 4 through pipe 7 and discharged into line 3. Hydrogen is withdrawn from storage 2 through line 5 and injected into the water stream. The mixture is then pumped by a booster pump 10 through a line 12, thence through a heat exchanger 14 where it flows in heat exchange relationship with the product, thence through line 16, thence through a fired coil or other suitable heating means 18, and eventually into the reactor 20 containing catalyst. At the inlet of the reactor 20 the nitro aromatic is injected into the preheated water-hydrogen stream through line 100 from storage container 1 by means of pump 101.

The catalyst we prefer to employ is molybdenum sulfide supported on charcoal, the molybdenum sulfide amounting to from 8-80% by weight of the catalyst composition, preferably around 10%. This catalyst may be in the form of pills, pellets, extruded lengths, and the like, and, as indicated in the drawing, the length of the beds of catalyst increase downwardly. The increase in depth of the catalyst beds provides means for equalizing the average contact time of the reactant with the catalyst throughout the bed, since of course as the reaction products proceed downwardly they become more diluted and require more time to complete the reaction. We prefer to feed all of the nitro aromatics into the top of the reaction zone, although provision has

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been made to inject them through line 102 into a multiplicity of mixing chambers 32, 34, and 36 along the length of the reactor. The nitro aromatic alone or in a mixture with amine product and/or water and/or other suitable diluent may be introduced at these various mixing chambers. The mixing chambers referred to are placed between the beds of catalyst, and the amount or fraction of the feed through any of the branch pipes 26, 28, and 30 may be individually controlled by valves or by operation of the proportioning orifices 40, 42, and 44.

Reaction products are withdrawn from the reaction zone through a line 50, passed through heat exchanges 14, thence passed through a cooler 52 and thence passed into a high pressure separator 54 from which the hydrogen-containing gas may be withdrawn overhead through line 56 and returned to storage 2. However, if the hydrogen is contaminated with impurities, (which is usually the case) a portion of the recycle gas should be vented from line 56 to the atmosphere through pipe 57 to maintain the desired hydrogen concentration. The amine product and water are withdrawn from high pressure separator 54 through a line 60 and discharged into a water separator 67 and finally delivered to storage 66. The water removed through line 62 is largely recycled back to the water tank 4 for reuse. Water formed in the reaction and any purge water introduced into tank 4 are discarded before recycling back to tank 4.

As is conventional in other operations, such as the hydrogenation of oil, the material withdrawn from high pressure separator 54 through line 60 is preferably passed through at least two stages wherein the pressure is reduced eventually to atmospheric pressure. For the sake of simplicity, we have omitted a showing of these pressure reducing stages since they are conventional and well known and do not go to the heart of the present invention.

As previously indicated, it usually will be necessary to inject additional gas, such as cold hydrogen gas, from line 5 through line 70 into manifold 74 and thence via branch lines 76, 78, and 80 into the reactor to counteract any tendency of the temperature therein to increase. The combined cooling effect obtained by heating this added gas to the temperature prevailing in the reaction zone plus the added water vapor absorbing capacity of the increased total gas within the reaction zone will tend to counteract effectively any sharp temperature increase in the reaction zone.

The flow of additional gas as required from line 74 directly into the reactor may be controlled manually or automatically by suitable and well known means, operating on the valves in line 74 and its branch lines 76, 78, and 80. Such valves are adjusted to maintain the desired temperature in said reaction zone. The important feature of our invention in this regard is to maintain an excess of liquid water at all times in the reaction zone.

Tests have shown that molybdenum sulfide catalyst supported on charcoal is not physically disintegrated by liquid water. Another catalyst found to be resistant to disintegration by water is platinum supported on activated carbon or charcoal. Certain of the catalysts, such as molybdenum sulfide on magnesia, clays, and the like, have been found to be unsatisfactory due to the fact that for some reason or other they undergo physical disintegration in a relatively short period of time.

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We shall now set forth a typical example illustrating our invention with the understanding that the precise conditions we are about to set forth are merely illustrative and do not impose any limitation on our invention.

A liquid mixture containing 20 volume per cent of nitro xylene and 80 per cent water enters the reaction chamber 20 with 3000 cu. ft. of hydrogen-containing gas saturated with water per barrel of 20-80 mixture. The inlet temperature to the reactor is 350° F. and a pressure of 3000 lbs. per square inch is maintained within the reactor, at which condition about 0.066 mol of water per mol of hydrogen is in the vapor state. The heat of hydrogenation of the nitro body increases the temperature of the mixture, but at the same time this temperature rise increases the capacity of the gas to absorb more water vapor. Without further addition of any cooling gas the reaction will go to about 35% conversion of the nitro xylene to xylidine before the temperature exceeds 450° F. Below or at this temperature cooling gas containing essentially no water vapor is injected via lines 76, 78, and 80. This added gas becomes saturated with water vapor at the reaction temperature by allowing vaporization of liquid water in the reaction zone. The sensible heat absorbed by the gas plus the latent heat absorbed by the water during vaporization combine to counteract a sharp temperature increase of the reaction mixture. We have found that to maintain the reaction temperature in the reaction zone at a value such that it does not exceed 450° F. there should be added approximately 4000 cu. ft. of hydrogen per barrel of nitro xylene-water feed. At 450° F. approximately 0.25 mol of water per mol of hydrogen will be in the vapor state. Since the ability of the gas to carry more water vapor increases rapidly with increase in temperature, it is therefore virtually impossible to attain excessively high reaction temperatures as long as vaporizable liquid is present.

As a modification of our invention, we may mix sufficient hydrogen from storage 2 with the nitro body and the water so that it will be unnecessary to add additional gas through line 72 to maintain the temperature in the reaction zone below the desired maximum.

Another modification of our invention involves further controlling temperature by recycling to the reaction zone a portion of the xylidine or other suitable diluent.

We may operate with recycle and cooling gas containing 25 to 100% hydrogen, although we prefer to operate with gas containing more than 50% hydrogen; at temperatures within the range of 350° F. to 450° F. or 500° F. in the reaction zone; pressures of from 500 to 5000 lbs. per square inch; feed rate of nitro body of from 0.1 to 0.8 volume of said nitro body per volume of catalyst per hour, and a water to nitro body ratio in the feed to the reactor such that the nitro body is diluted from 1 to 10 or 12 times. We may use any other volatile liquid in place of water. Also we prefer to re-use water since it will contain some dissolved amine body and the tendency for further dissolving of the amine body will thus be repressed.

To recapitulate briefly, our invention relates to controlling chemical reactions of exothermic nature to prevent sharp temperature increases and to maintain the reaction mass below the desired maximum. It is a matter of record of course to accomplish this result by evaporative cooling using water, generally speaking, and with

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reference to chemical reactions broadly. But our invention involves maintaining an excess of water in the reaction zone and injecting into the zone gas which has the capacity to absorb water vapor, and even though high pressures are employed and the normal amount of water absorbed by the gas is relatively low at the temperature it enters the reaction zone, nevertheless this capacity to absorb water increases sharply as the temperature of the gas increases so that the cooling effect obtained by the evaporation of water at higher temperatures is sufficient to counteract sharp temperature increases and to maintain with certainty the reaction mass below the desired maximum.

What we claim is:

1. The method of continuously reducing aromatic compounds to the corresponding aromatic amines which comprises providing a reaction zone containing a plurality of spaced beds of a hydrogenation catalyst, continuously introducing into the top of the reactor an aromatic nitro compound, hydrogen and a large quantity of liquid water, causing said mixture to flow through the reaction zone whereby at least a portion of the aromatic nitro compound is reduced to the corresponding aromatic amine, injecting additional hydrogen gas into the reaction zone at points spaced between the catalyst beds whereby the vaporization of the water is accelerated and whereby the tendency for the reaction temperature to exceed a desired maximum is retarded, maintaining a temperature between 400° and 500° F. and pressures above the vapor pressure of the water at the reaction temperature, maintaining sufficient water in said reaction zone to absorb excess heat by vaporization of the water, the water being in such excess that some liquid water is maintained in the reaction zone and recovering aromatic amines and water from the reaction zone.

2. The method of continuously reducing mononitroxylene to xylidine which comprises providing a reaction zone containing a plurality of spaced beds of hydrogenation catalyst, continuously introducing into the top of the reactor nitroxylene, hydrogen and a large quantity of liquid water, causing said mixture to flow through the reaction zone whereby at least a portion of the nitroxylene is reduced to xylidine, injecting additional hydrogen gas into the reaction zone at points spaced between catalyst beds whereby the vaporization of the water is increased and whereby the tendency for the reaction temperature to exceed a desired maximum is retarded, maintaining a temperature between 400 and 500° F. and pressures above the vapor pressure of the water at the reaction temperature, maintaining sufficient water in said reaction zone to absorb excess heat by vaporization of the water, the water being in such excess that some liquid water is maintained in the reaction zone and recovering xylidine and water from the reaction zone.

3. A method according to claim 2 in which the amount of water present is approximately 10 volumes per volume of mononitroxylene and in which the amount of hydrogen added to the reactor is 4,000 cubic feet per barrel of mononitroxylene.

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