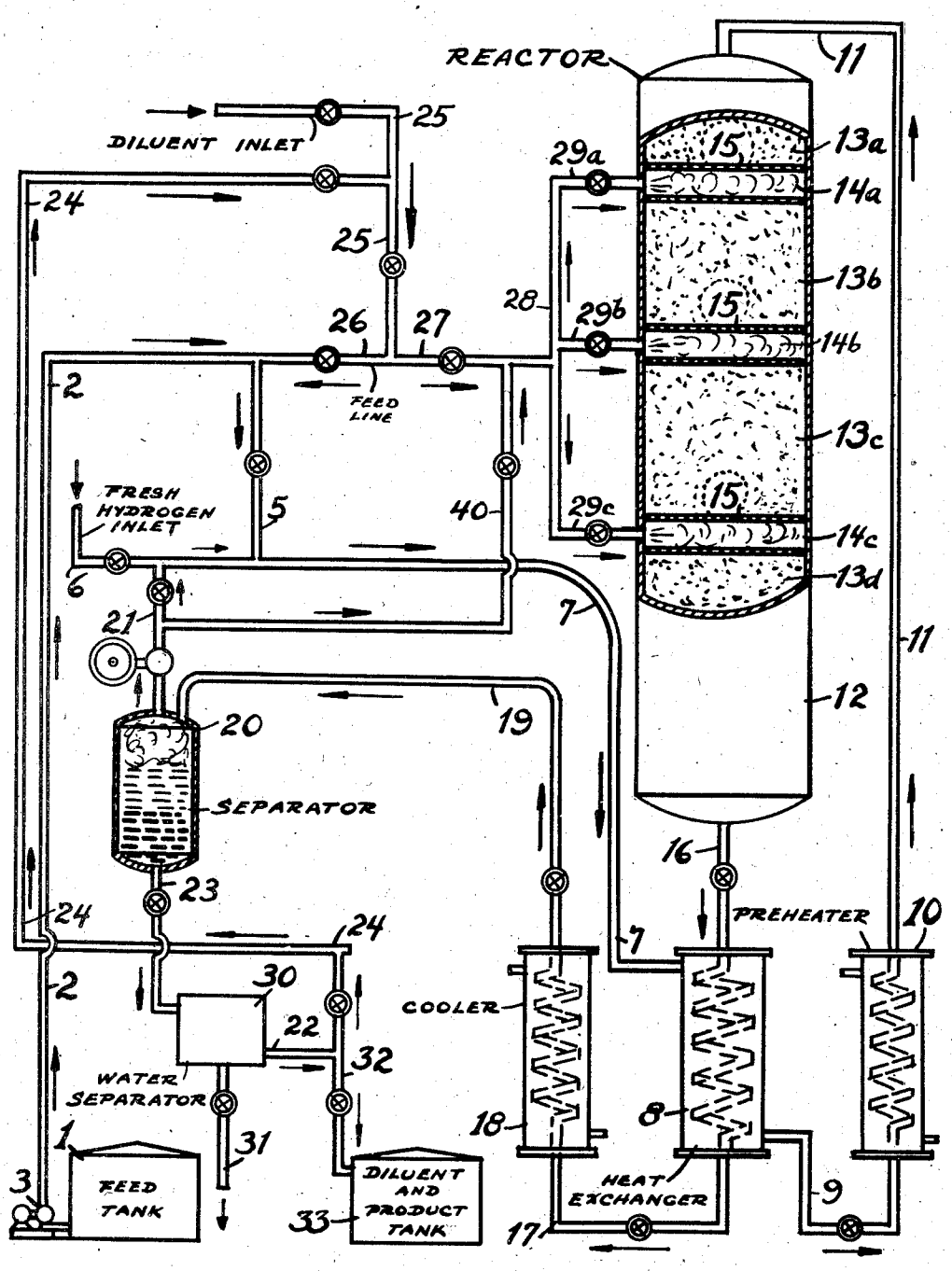
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METHOD OF PREPARING AMINES

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Edwin J. Gohr Inventor

By P. L. Yeomans Attorney

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METHOD OF PREPARING AMINES

Edwin J. Gohr, Summit, N. J., assignor to Standard Oil Development Company, a corporation of Delaware

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1 Claim. (Cl. 260—580)

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This invention relates to the improvements in the manufacture of aromatic amines and, more particularly, it relates to a method for controlling the catalytic reduction of nitro aromatics such as nitro xylenes to form the corresponding amino compounds.

It has been known for a long time that certain amines, particularly the aromatic amines such as xylidene, are very valuable blending agents for aviation gasolines. These compounds have the property of improving the characteristics of the aviation fuel, particularly its rich mixture performance, during the period when the airplane is taking off from the ground or is suddenly accelerated in flight. When an airplane is in flight at a fairly constant rate of speed, a lean mixture of fuel and air is required for desirable combustion performance. Such a mixture contains preferably about 0.065 pound of fuel per pound of air. However, it often becomes necessary for the plane to suddenly develop more power, such as when taking off from the ground, climbing suddenly in the air, and in other flight maneuvers.

During such times the fuel-air ratio greatly exceeds that desired for lean mixture performance, and in such a case, the ratio is usually from about 0.9–0.12 pound of fuel per pound of air.

There has recently been developed a method for testing the rich mixture performance of an aviation gasoline. This method is known as the A. F. D.–3C test. This test determines what is commonly known as the "indicated mean effective pressure" (I. M. E. P.). An aviation gasoline containing 4 cc. of lead tetraethyl per gallon, having an octane number of 100, and a rich mixture performance, which matches a reference fuel known as S+1.25 cc. of lead, or in other words, an indicated mean effective pressure according to the A. F. D.–3C test of approximately 200 pounds per square inch, meets current specifications for 100 octane aviation gasoline. When, however, small volumes of certain amino aromatic compounds such as xylidene are added to such a 100 octane gasoline, its rich mixture performance is considerably increased. Thus, the utility of the aromatic amines as addition agents to aviation gasoline is obvious.

According to the present invention the aromatic amines are prepared by catalytically reducing nitro aromatic compounds under closely controlled conditions of temperature, pressure and feed rate of charging stock, so as to produce maximum quantities of desired amines of good quality. If the nitro aromatic compounds contain appreciable amounts of the dinitro and/or some trinitro derivatives, the hydrogenation or reduction of these compounds to amines may be a highly hazardous reaction at temperatures above 500–600° F., due to the ease at which these polynitro compounds decompose at elevated temperatures.

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The present invention has for its main object a method for preparing aromatic amines continuously in economical and otherwise commercially feasible manner.

A more limited object of this invention is to provide a method for overcoming the hazards encountered in the reduction of the nitro compounds to amines, particularly when polynitro derivatives are present.

According to the present invention, these and other objects are obtained by introducing large amounts of a heavy diluent into the reactor in which the nitro compounds are undergoing reduction in the presence of the catalyst. This diluent should be sufficiently high boiling to remain in the liquid state and thus retain in solution dinitro or heavier nitro compounds should the mononitro be wholly or partially vaporized at some point in the operation. The heat capacity of the diluent will also prevent rapid temperature changes or hot spots in the reactor tending to cause decomposition. The diluent thus introduced reduces the tendency of these compounds to concentrate whereby decomposition or detonation might take place. Even when little or no nitro compounds higher than mono are present, a diluent may be used in order to provide heat capacity for absorbing sudden temperature rises, uneven temperature distribution and the like, whereby undesirable decomposition of the mono compound will be avoided.

For illustration, one concrete embodiment of this invention is shown in the somewhat diagrammatic flow chart comprising a single view of the accompanying drawing.

Referring to this drawing, liquid nitro compounds, such as nitro xylene isomers, containing about 10% of the dinitro derivatives, are fed from storage vessel 1 through line 2 and are pumped by pump 3 through line 5 and mixed with hydrogen entering from lines 21 and 6. It is desirable to circulate between 5000 and 70,000 preferably about 45,000 cu. ft. of hydrogen per barrel of nitro compound through the reactor. The mixture of hydrogen and nitro compounds is passed through line 7 through heat exchanger 8. From this heat exchanger, the mixture of nitro compounds and hydrogen is passed through line 9 into preheater 10 where it is heated to a temperature of 300–400° F. and passed through line 11 into the top of reactor 12.

Reactor 12 comprises a plurality of catalyst chambers diagrammatically represented at 13*a*, 13*b*, 13*c* and 13*d*, the catalyst being supported on porous plates, such as screens 15. These catalyst chambers are separated by spaces 14*a*, 14*b* and 14*c* which serve as mixing chambers. The catalyst in each of these chambers may be any desired hydrogenation catalyst, but because of its good physical strength a very suitable catalyst has been

found to be 5–80%, preferably 10%, of molybdenum sulfide deposited on charcoal; tungsten sulfide; a mixture of 1 part nickel and 2 parts of tungsten sulfide; molybdenum oxide and/or zinc oxide with magnesium oxide; and molybdenum sulfide; nickel or nickel sulfide supported on alumina, silica, porcelain, or charcoal; copper oxide on alumina, and the like.

The mixture of heated nitro compounds and hydrogen introduced into the topmost chamber 13*a* immediately undergoes reaction whereby the nitro compounds are reduced by the hydrogen with the liberation of large quantities of heat. Temperatures in the reactor are maintained between 350 and 600° F., preferably about 450° F. Pressures may range from 500 to 5000 lbs./sq. in. The mixture of hydrogen, reduced nitro compounds and unreacted nitro compounds is passed down through the reactor successively into each of the chambers 13*b*, 13*c* and 13*d*, in the latter of which the reaction is completed.

It should be noted that the catalyst beds are shown becoming longer as the reactant passes through the reactor. This feature is an important one in the working of this process in that compensation is allowed for the ever increasing dilution of the charge with product from the previous stage. This allows more contact time at the greater dilution which is required to maintain the same degree of conversion at a definite temperature level. However, this feature should not be considered as limiting the invention, as any other type of reactor can be used as desired.

Products of the reaction are withdrawn from the bottom of the reactor through line 16 and are passed through heat exchanger 8 in heat exchange relation with the incoming mixture of hydrogen and nitro compounds being fed into the topmost catalyst chamber. The reaction products leave the heat exchanger through line 17 and are passed to cooler 18 where they are still further reduced to a temperature at which the products condense. From cooler 18 the products pass through line 19 into separator 20. In this separator, the unreacted gases are separated from the products and since they contain a large amount of unreacted hydrogen, they are removed through line 21 and recycled to the system through lines 7 and 40.

As mentioned above, appreciable quantities of polynitro derivatives are usually present in the feed introduced to the reactor through line 11. These derivatives may decompose violently at temperatures not greatly in excess of those required for reduction. According to this invention, the hazards connected with the presence of these polynitro compounds are overcome by passing the nitro compounds in line 2 to line 5 where they are contacted with a diluent entering through lines 25 and 26. Diluent from line 25 may also be injected into the reactor through line 27 with or without hydrogen from line 40 and thence to a plurality of points such as, for example through lines 29*a*, 29*b* and 29*c*. While the diluent may be introduced at any point along the reactor, it is preferable to introduce this mixture in the spaces between several catalyst beds, such as for example, at 14*a*, 14*b* and 14*c*. The amount of diluent added through line 26 may vary greatly, but preferably should be from 20–90% by volume of the total liquid mixture fed into the reactor 12. The mixture of nitro aromatic compounds and diluent is passed through line 5 and thence through 7 into the system.

Suitable diluents may be lubricating oil, gas oil, white oil, kerosene, or any other hydrocarbon diluent boiling above about 500° F. Such a diluent will act to reduce the hazard incident to the presence of the polynitro compounds. Since the nitro compounds are more easily reduced than any of the above diluents, the diluent will remain unchanged throughout the reaction.

The amines obtained by the reduction are withdrawn together with the heavy diluent through line 16, passed through heat exchanger 8 and cooler 18 into separator 20 where hydrogen for recirculation is separated as described above. The reaction products and diluent are removed through line 23 and passed to water separator 30 from which water is removed through line 31. The amines and diluent are removed through line 22 and passed to storage tank 33 through line 32. If desired, some of the reaction product withdrawn through line 22 may be recycled to the system through line 24. Diluent may be separated from the amines by distillation and the former returned to the operation through line 25.

The nature and objects of the present invention having thus been set forth and a specific embodiment of the same given, what is claimed as new and useful and desired to be secured by Letters Patent is:

A method of continuously reducing aromatic nitro compounds which comprises maintaining a reaction zone containing a plurality of spaced beds of a catalyst consisting essentially of molybdenum sulfide on charcoal, introducing into one of said beds of catalyst in said reaction zone, a mixture of aromatic nitrocompounds, a heavy oil diluent which is sufficiently high-boiling to remain in the liquid state and hydrogen, causing said mixture to flow through the said bed of catalyst whereby at least a portion of the aromatic nitro compound is reduced to the corresponding amine, injecting a mixture of heavy oil and aromatic nitro compound into the reaction zone at points between the spaced beds of catalyst, causing the latter-introduced mixture of heavy oil and aromatic nitro compound to flow through the beds of catalyst at a temperature between 350 and 600° F. and pressures between 500 and 5000 lbs./sq. in. to cause reduction of the nitro aromatic compound to the corresponding amine, maintaining sufficient heavy oil in said reaction zone by the injection of said oil to prevent the temperature prevailing in the reaction zone from exceeding a desired maximum and recovering amino aromatics from said reaction zone.

EDWIN J. GOHR.

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